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THE OCCURRENCE OF CADMIUM IN SEAWATER AND IN MARINE ORGANISMS AND SEDIMENTS

By

J. B. MULLIN and J. P. RILEY
Department of Oceanography, University of Liverpool

ABSTRACT

Methods have been developed for determining cadmium in seawater, marine organisms, and marine sediments. The procedure, based on the dithizone extraction method of Saltzman, is capable of detecting less than 10 mμg of the element and can be used for determining cadmium in silicate rocks; only thallium interferes. To confirm the presence of cadmium and to ensure freedom from contamination, the dithizone extracts were examined spectrographically.

The average cadmium concentration found in waters of the Irish Sea and of the English Channel was 0.113 μg/l (1.0 μg at/m^3), with values ranging from 0.024 to 0.25 μg/l (0.21–2.2 μg at/m^3) depending upon position and season. It is probable that the variations are due to adsorption or utilization of the element by plankton outbursts or to adsorption by detritus.

The occurrence of cadmium in several marine plants and animals (dried at 110°) has been observed and the concentration varied between 0.134 (*Laminaria digitata*) and 16.4 μg/g (*Patella vulgata*). The distribution of the element in various organs of *Pecten maximus*, *Buccinum undatum*, *Chlamys opercularis*, and *Porania pulvillus* has been investigated. Cadmium in calcareous shells is usually less than 0.02 μg/g, muscle contains about 1.5 μg/g, and high concentrations (up to 500 μg/g) are found in the digestive glands and renal organs of molluscs.

A representative selection of marine sediments has been analysed; the mean values of cadmium for diatomaceous oozes (0.39 μg/g), globigerina oozes (0.42), and radiolarian oozes (0.45) are close to the average value reported by Goldschmidt for the concentration of cadmium in the upper lithosphere. Two manganese nodules

contained 8.4 and 5.1 μg/g of cadmium respectively; thallium (*ca* 2 μg/g) was also detected in each case.

INTRODUCTION

In a recent note (1) the authors have given a preliminary description of the detection of cadmium in seawater; it is the purpose of this paper to amplify this account and to describe studies of the cadmium contents in a number of marine organisms and sediments.

Neither Bardet *et al* (2) nor Noddack and Noddack (3) were able to detect cadmium spectrographically in seawater, and the latter workers consider that its concentration must be less than 0.5 μg/l. Goldschmidt (4) has reviewed the geochemistry of the elements and has quoted average figures of 80, 0.18, and 0.5 μg/g for the abundances of zinc, cadmium and mercury respectively in the lithosphere. The concentrations of zinc (3, 5, 6) and mercury (3) in seawater are 8–20 and 0.3 mg/m^3 respectively. Buljan (7), who has compared the terrestrial abundances of elements with their concentrations in seawater by plotting their concentrations (as log gm-at/ton) against their atomic numbers, has found certain regularities among members of the same group of the periodic table. His results, when corrected for an erroneous mercury concentration, indicate that the concentration of cadmium in seawater should be *ca* 1.8 mg/m^3. Ishibashi and Shigematsu (8) have predicted the abundances of most of the elements in seawater from a relationship between log (percentage of the element in the lithosphere/percentage of the element in seawater) and ionic potential of the element. They concluded that seawater contains 0.045 μg Cd/l.

The concentration of metals from seawater by organisms is well known. The first record of the occurrence of cadmium in the animal kingdom is due to Fox and Ramage (9) who detected the element spectrographically in the livers of 11 separate specimens of the lamellibranch, *Pecten maximus*. Noddack and Noddack analysed 10 sea organisms spectrographically and reported cadmium concentrations ranging from 0.03 to 11 μg/g in the dried specimen (for the shell of an echinoid, *Brissopsis lyrifera*, and a whole jellyfish, *Cyanea capillata* respectively). Malyuga (10) has determined cadmium polarographically in a number of sea animals and plants, finding 0.1–1 μg/g in dried algae and 1.1 μg/g in *Asterias rubens;* in the other sea animals examined cadmium was just detectable.

Most of the other studies (11, 12, 13, 14, 15) of trace elements in marine organisms have been carried out on algae, but cadmium has been rarely reported, perhaps due to its concentration being normally below the limits of direct spectrographic detection.

The geochemistry of cadmium is as yet incompletely known; arely does the element seem to be enriched in igneous rocks, in which he abundance ratio Zn : Cd is *ca* 900 : 1. Practically no data are vailable on the occurrence of cadmium in sedimentary rocks, but ince its ionic radius in octahedral co-ordination (1.03A) is practically dentical with that of calcium (1.06A) and since zinc and cadmium arbonates (Smithsonite and Otavite) are isomorphous with calcite, Goldschmidt (17) has considered that in small amounts they may eplace calcium in carbonate sediments. Both of these elements ccur in considerable amounts (up to 0.3% Zn and 0.01% Cd) in the narine phosphorites of organic origin of the South Sea Islands (16). Goldschmidt (17), who has discussed the fate of cadmium in marine ydrolysates such as muds and clays, has stated that it may be leached rom the hydrolysate, like calcium, or be incorporated in the clay inerals by ion exchange because of its ability to form tetrahedral onds. Owing to its large ionic radius, its ability in the latter direc- ion is likely to be much more restricted than zinc.

Development of a Method for Determining Cadmium in Seawater. ince the concentration of cadmium in seawater is below the limits f direct detection, a preliminary concentration of the element is ecessary. The use of dithizone extraction for this purpose has been nvestigated from the theoretical standpoint by Koroleff (18). Cad- nium can be extracted quantitatively from solutions more basic than H 6.5 by using a solution of dithizone in chloroform. A solution f dithizone in carbon tetrachloride has been used (19) as the sta- ionary phase on a cellulose acetate column in a partition chromato- raphic method for the separation of certain trace metals (including admium) from seawater.

A review of the literature indicated that the dithizone extraction nethod described by Saltzman (20) offered the greatest prospect or success. In this procedure cadmium is extracted with a chloro- orm solution of dithizone in the presence of hydroxylamine hydro- hloride from a strongly alkaline solution (*ca* 1.6 N in NaOH) con- aining tartrate and cyanide to minimise the extraction of interfering lements. The cadmium is extracted from the chloroform layer by neans of tartaric acid. The aqueous layer is then made strongly lkaline with sodium hydroxide, and the cadmium is re-extracted ith dilute dithizone in the presence of hydroxylamine and a small oncentration of cyanide. The optical density of the extract is easured at 518 mμ, the wavelength of maximum absorption of admium dithizonate. Quantities of cadmium as low as 5 μg can be etermined in the presence of at least 1000 times as much silver,

bismuth, copper, cobalt, iron, manganese, lead, tin and zinc and of 20 times as much mercury; thallium alone interferes. Saltzman's procedure is not directly applicable to seawater since the alkalinity used in the first dithizone extraction would lead to the precipitation of calcium carbonate and magnesium hydroxide.

Experiments were carried out to extract cadmium at a concentration of 0.5 μg/l from both distilled water and seawater buffered to pH 8.3 or 6.5 by means of ammonium chloride and sodium hydroxide; sodium citrate was added to prevent the precipitation of the hydroxides of iron and aluminium. The determination was carried out as described on p. 108. In each case recoveries of over 97% of the added cadmium were obtained and in all further work the preliminary extraction was carried out at pH 8.3.

Effect of Foreign Ions. Since dithizone is not a specific reagent and will in fact form chloroform extractable complexes with 17 elements (21), the combined effect of these elements was examined at 25 times their maximum recorded concentrations in seawater (*viz* Hg^{2+} 10; Cu^{2+} 250; Zn^{2+} 250; Pb^{2+} 100; Mn^{2+} 125; Co^{2+} 5; Ni^{2+} 10; Bi^{2+} 10; Ag^{2+} 10 μg/l). It was found that the optical density (at 518 mμ in a 4 cm cell) of the final dithizone extract was only 0.012 greater than the reagent blank; therefore the interference of these elements at their seawater concentrations is negligible. Since the method was also applied to marine sediments, the effects of a number of these elements at higher concentrations were investigated, with the following results:

Element	Cu^{2+}	In^{3+}	Pb^{2+}	Hg^{2+}	Tl^{+}	Zn^{2+}
Concentration (μg/l)	500	10	500	100	10	500
Optical density*	0.009	0.002	0.017	0.000	0.057	0.025

* Measured at 518 mμ in a 4 cm cell, reagent blank deducted.

The only appreciable interference at low concentrations is caused by thallium, which has not yet been detected in seawater but which is concentrated to a slight extent by marine organisms (3). The concentration of the element in marine sediments is not likely to exceed 2 μg/g. Thus it is improbable that it is a source of error in the present work, but, to guard against this, all dithizone extracts were examined spectrographically, and in only two cases (both manganese nodules containing thallium) has any other dithizone-extractable element, save cadmium, been detected.

Determination of Cadmium. In order to test the modified method varied amounts of cadmium were added to one litre samples of metal

ree water and extracted as described elsewhere. The optical densities f the final dithizone extracts (final volume 7 ml), measured at 518 nμ in 4 cm cells, were:

Wt. of cadmium (μg)	0.1	0.2	0.3	0.5	1
Optical density	0.041	0.082	0.118	0.197	{0.401
[less reagent blank (0.033)]					{0.408

EXPERIMENTAL

Reagents. All reagents and solutions were prepared with water reshly distilled from a silica still. All chemicals used were of analy-ical reagent grade.

(1) Standard cadmium solution (10 mg/l). Dissolve pure cadmium 10 mg) in 3 ml of nitric acid (30% v/v). Evaporate the solution to dryness on a waterbath. Take up the residue in 0.5 ml of 60% perchloric acid and fume to dryness under a Vitreosil infra-red heater. Dissolve the product in water and dilute to 1 l. This stock cadmium olution was diluted as required for calibrating the extraction method.

(2) Ammonium chloride 1 N (53.5 g/l). Preserve in a polyethylene ottle.

(3) Potassium cyanide (2.5%). Dissolve 2.5 g of potassium cyanide n 100 ml of water. Store in a polyethylene bottle and dispense rom a 10 ml tilt measure.

(4) Tartaric acid (20 g/l). Store in the refrigerator and reject f growth of mould has commenced.

(5) Sodium citrate (100 g/l).

(6) Hydroxylamine hydrochloride (2.5 g/25 ml). Prepare fresh eagent each week.

(7) Sodium hydroxide-potassium cyanide reagent. Dissolve sodium ydroxide (40g) in 70 ml of water. When cool, add a solution of .05 g of potassium cyanide in 5 ml of water and dilute to 100 ml. tore in a polyethylene bottle.

(8) Dithizone reagents. The dithizone was supplied by British Drug Houses. The chloroform employed conformed to the British Pharmacopeia specification; it was recovered after use, as described y Mullin and Riley (22).

(a) Extraction dithizone. Prepare a solution of dithizone in chloroform containing 120 mg/l and store in a dark glass bottle in the refrigerator.

(b) Standard dithizone. Dilute 5 ml of the extraction dithizone to 100 ml with chloroform. Store in the refrigerator. Slight variations in the strength of the reagent were of no account, but it was prepared freshly fortnightly.

(9) Nitric acid. Redistil pure concentrated nitric acid from an all glass still.

(10) Perchloric acid (60% w/w).

(11) Hydrofluoric acid (40% w/w).

Determination of Cadmium in Seawater. The filtered (Whatma No. 2) seawater (950 ml) was placed in a one litre glass-stoppere short-stemmed separating funnel, followed by 10 ml of 1 N ammoniun chloride, 25 ml of sodium citrate solution, and 10 ml of 2.5% potas sium cyanide solution. The mixture was extracted by shaking fo five minutes with 15 ml of extraction dithizone. The chloroforn layer was run into 10 ml of 2% tartaric acid contained in a short stemmed 50 ml separating funnel. The seawater was re-extracte with an additional 15 ml of extraction dithizone. The combine chloroform extracts were shaken vigorously with the tartaric acid fo two minutes and the lower layer was then discarded. The aqueou layer was washed with 3 ml of pure chloroform; the lower layer wa carefully rejected, and any drops of chloroform floating on the surfac were removed with a gentle current of air.

The tartaric acid layer was treated with 0.25 ml of hydroxylamin hydrochloride solution, made alkaline with 2.5 ml of sodium hy droxide-potassium cyanide reagent; then 7.0 ml of standard dithizon were added from a pipette. The separating funnel was shaken vigo ously for one minute. The lower layer was separated and then drie by passing it through a dithizone-extracted chloroform-washed plu of ashless filter paper in the stem of a 2.5 cm funnel. The optic density of the extract was measured at 518 mμ in a 4 cm cell. Th reagent blank was determined by using 950 ml of water distille from glass or quartz apparatus. A calibration curve was prepare by carrying out the determination with known amounts of cadmiu in distilled water. In later work, two litre samples of seawater we analysed in order to increase the accuracy of the determination; th same quantities of reagents were employed except that the fir extractions were carried out with 25 ml of extraction dithizon

Determination of Cadmium in Biological Materials. It was foun that dry ashing of biological materials, even at temperatures as lo as 400°, could lead to losses of up to 50% of the cadmium presen Cadmium was therefore determined after destruction of the organ matter with nitric acid (23).

The weighed, air-dried sample (0.5–5 g) was placed in a 250 r conical flask, and 15 ml of 30% v/v nitric acid were gradually adde The neck of the flask was closed with a loosely fitting bulb stopp in the side of which a hole had been blown to allow vapours to escap

The flask was heated on a hot plate, from which it was removed if the reaction threatened to become violent. When all foaming had ceased, continuous heat was applied until the mixture was evaporated to dryness. A second evaporation was carried out with another 5 ml of 30% v/v nitric acid; this was followed by repeated evaporations with 15 ml volumes of concentrated nitric acid until all carbonaceous matter had been oxidized. Normally not more than three evaporations with concentrated nitric acid were necessary to give a white residue (some organisms yielded residues stained brown with iron salts). The salts were washed into an evaporating basin with a jet of water and evaporated to dryness. The residue was taken up in 5 ml of water, and 0.5 ml of 60% perchloric acid was added; the liquid was evaporated under a Vitreosil infra-red heater until no further acid fumes evolved. The residue was digested on the water bath with 200 ml of water containing 2.5 ml of concentrated hydrochloric acid. The solution was filtered through an ashless filter paper and diluted to 250 ml. A suitable aliquot of this solution was placed in a one litre separating funnel, diluted to *ca* 950 ml, and treated with 25 ml of 10% sodium citrate solution. The pH was adjusted to *ca* 9 (phenolphthalein) by addition of 2N sodium hydroxide. Cadmium was determined in the solution as in the case of seawater. Good recoveries of added cadmium (over 98%) were obtained and the method showed a standard deviation of 1.5%.

Determination of Cadmium in Sediments. The sediment (1 g) was weighed into a platinum basin which was then covered with a clock glass; 2 ml of concentrated nitric acid were gradually added. When all effervescence had ceased, the watch glass was rinsed and removed and 30 ml of 40% hydrofluoric acid were added; the mixture was evaporated to dryness on the water bath. In the case of Green Mud, further evaporation with nitric acid was necessary to decompose organic matter. The residue was then dissolved in a small quantity of distilled water, 1 ml of 60% perchloric acid was added, and the solution was evaporated under an infra-red heater until all fumes of perchloric acid had ceased. The dried product was extracted with 2.5 ml of concentrated hydrochloric acid and treated with 150 ml of distilled water; the resultant solution was filtered through an ashless filter paper. After the solution had been diluted to *ca* 950 ml and its pH adjusted to *ca* 8, by the careful addition of sodium hydroxide, cadmium was determined as described for seawater. An exactly analogous blank determination was made in the same manner, omitting the sample. The method, which shows a standard deviation of 2.5%, has approximately ten times the sensitivity of the procedure described by Sandell (24).

Determination of Cadmium in Manganese Nodules. The finely powdered nodule, dried at 110° (1.0 g), was placed in a silica basin and covered with a watch glass; 5 ml of concentrated hydrochloric acid were added. After standing overnight, the mixture was evaporated to dryness under an infra-red heater. The residue was treated with 100 ml of 2.5% hydrochloric acid, and after solution of the salts by warming, the insoluble matter was removed by filtration through an ashless filter paper. The latter was washed well and ignited in a platinum crucible in a muffle furnace at 800° C; silica was volatilised from the cold residue by addition of 5 ml of 40% hydrofluoric acid and one drop of concentrated sulphuric acid. The liquid was evaporated to dryness and the residue was heated to a dull redness. The resultant oxides were fused with 2 g of potassium bisulphate and the cold mass was dissolved in water. After filtration, this solution was added to the main bulk of the solution of the nodule and diluted to *ca* 900 ml. The solution was brought to *ca* pH 8 by the addition of sodium hydroxide, and 10 ml of 2% hydroxylamine hydrochloride were added to avoid oxidation of dithizone by ferric iron or manganese (III). Cadmium was extracted with four 15 ml portions of extraction dithizone in the presence of citrate, cyanide, and ammonium chloride, as described for seawater. The reagent blank was determined in the same manner, but omitting the manganese nodule.

Spectrographic Analysis. In order to obtain unequivocal proof of the presence of cadmium in the materials analysed, the dithizone extracts were examined spectrographically. Such examination also had the advantage of determining whether or not the extracts were free of other elements. The technique used was a modification of the method of Wark (25), who evaporated dithizone concentrates onto graphite powder prior to spectrographic analysis. We have found that the sensitivity of detection can be considerably increased by evaporating the extract on spectrographically pure calcium carbonate instead of graphite.

Detection Method. A dropping pipette was constructed by fusing a thistle funnel of *ca* 10 ml capacity to one end of a piece of 1.5 mm bore capillary tubing. The latter was drawn out at its lower end to a fine capillary of such dimensions that it had a drop time of 2–2.5 seconds when the upper bulb was filled with chloroform. "Specpure" calcium carbonate (2 mg) was placed in a one ml microcentrifuge cone and the latter was immersed to a depth of 2 cm in a water bath at 90–95°. The tip of the dropping pipette was inserted into the centrifuge tube so that it rested against the side at approximately 1.5 cm from the top of the calcium carbonate. The dithizone extract to be examined was placed in the thistle funnel and allowed to flow

onto the calcium carbonate at such a rate that there was never a greater depth than 1 mm of unevaporated chloroform in the centrifuge cone. The dry calcium carbonate carrying the dithizonate was packed into a cavity in a 6.25 mm graphite electrode and burnt in the D.C. arc at a current of *ca* 5.7 amps against a graphite cathode. The spectrum was recorded on Ilford Ordinary plates, using a medium quartz spectrograph. Falling plate studies showed that the cadmium lines had their greatest intensity in the first 10 seconds of arcing; thereafter the intensity fell off rapidly owing to loss of cadmium by volatilization. Therefore the exposure given was 10 seconds. Tests with known amounts of cadmium showed that Cd 2288.018A was quite clearly visible with 5 mμg of cadmium, Cd 3261.057A was very faint with this amount of the element, and Cd 2265.017A was visible only if more than 10 mμg of cadmium were present.

RESULTS

Seawater. Sea surface samples were collected at a number of stations in the Irish Sea and in the English Channel off Plymouth, using a wooden or canvas bucket. The samples, stored in five litre polyethylene bottles, were analysed as soon as possible after collection. Experiments showed that the concentration of cadmium in filtered seawater stored in polyethylene containers did not change over a period of at least five weeks. Earlier work indicated a much higher concentration of cadmium in seawater than was found subsequently; this discrepancy was traced to contamination of the water by cadmium leached from the soft glass "salinity" bottles in which samples had been stored.

The samples were analysed as described on p. 108; the results are shown in Tables I, II and III. With the later samples, analyses were carried out on volumes of two litres in order to increase the accuracy of the determination, the amounts of dithizone used in the first extraction being increased proportionately. Duplicate determinations, carried out on a number of samples, showed good agreement (*viz* Table III).

TABLE I. Occurrence of Cadmium in the Surface Waters of the Irish Sea

Lat. (*N*)	*Long.* (*W*)	*Date*	μg Cd/*l*	*Date*	μg Cd/*l*	Cl °/₀₀
53° 26′	4° 16′	27.4.54	0.034	23.11.54	0.080	18.63
53° 24′	4° 52′	27.4.54	0.081	24.11.54	0.159	17.99
54° 16′	4° 49′	10.5.54	0.050	7.12.54	0.122	18.91
53° 52′	4° 17′	16.5.54	0.060	7.12.54	0.118	18.43
54° 02′	4° 51′	12.5.54	0.060	15.12.54	0.045	18.59
53° 50′	4° 09′			15.12.54	0.080	18.67
		Mean	0.057		0.101	

TABLE II. Occurrence of Cadmium and Copper in the Surface Waters of the Irish Sea

Lat. (*N*)	*Long.* (*W*)	*Date*	Cl °/₀₀	*μg* Cd/*l*	*μg* Cu/*l*
54° 3′	4° 36′	2.5.55	18.83	0.200	11.5
53° 57′	4° 23′	2.5.55	18.86	0.083	8.7
53° 53′	4° 06′	2.5.55	18.86	0.252	17.3
53° 44′	3° 52′	3.5.55	18.50	0.198	15.6
53° 40′	3° 36′	3.5.55	18.23	0.137	14.0
53° 34′	3° 20′	3.5.55	17.91	0.127	15.0
		Mean		0.166	13.7

The mean cadmium concentration, considering all samples given in Tables I, II and III, was 0.113 μg/l (1.0 μg at/m³), a value which is in reasonable agreement with that predicted by Ishibashi and Shigematsu (0.045 μg/l) but which is considerably less than the amount suggested by Buljan (1.8 μg/l).

The data show, however, that the cadmium concentration is variable and that as much as a threefold variation may be found over quite a small area. Similar differences have been found (26) in the copper concentration at certain of these stations (*cf* Table II). These variations may well be caused by adsorption (27, 28) or by utilization

TABLE IV. Occurrence of Cadmium in Marine Algae

Organism	Cd *μg/g*	*Concentration factor* × 10^{-3}*
Chlorophyceae		
Codium sp. (Codiaceae)	0.865	7.6
Halimeda gracilis (Codiaceae)†	0.312	2.7
Phaeophyceae		
Ascophyllum nodosum (Fucaceae)	0.349	3.1
Fucus serratus (Fucaceae)	0.792	7.0
F. vesiculosus (Fucaceae)	2.03 2.08	18.1
Pelvetia canaliculata (Fucaceae)	0.500 0.508	4.5
Laminaria digitata (Laminariaceae)	0.134	1.2
Rhodophyceae		
Lithophyllum sp. (Corallinaceae)‡	0.358	3.2
Corallina officinalis (Corallinaceae)	0.858	7.6
Lithothamnion sp. (Corallinaceae)	0.844	7.4

† From Gulf of Manaar (Indian Ocean).

‡ Origin unknown; sample analysed by method used for silicates.

* Concentration factor = concentration of cadmium in air dried organism/mean concentration of cadmium in seawater (0.113 μg/l).

TABLE III. Occurrence of Cadmium in the Surface Waters of the English Channel

Lat. (*N*)	*Long.* (*W*)	*St.*	*Date*	*μg* Cd/*l*	*Date*	*μg* Cd/*l*	*Date*	*μg* Cd/*l*	Cl °/₀₀
50° 20′	4° 10′	L2	11.7.54	0.076 0.079	11.10.54	0.072	16.2.55	0.241	16.64
50° 18′	4° 11′	L3	11.7.54	0.058	11.10.54	0.057	16.2.55	0.189	18.45
50° 15′	4° 13′	L4	11.7.54	0.150 0.163	11.10.54	0.072	16.2.55	0.126	19.22
50° 15′	4° 18′	L5	11.7.54	0.124	11.10.54	0.072	16.2.55	0.171	19.36
50° 06′	4° 21′	L6	19.7.54	0.040	11.10.54	0.064	16.2.55	0.256	19.48
50° 02′	4° 22′	E1	19.7.54	0.024	11.10.54	0.146	16.2.55	0.094	19.54
			Mean	0.096		0.081		0.180	

of both elements by localised communities of plankton which are well known to occur in these waters. It is interesting to note that seawater containing the lowest concentration of cadmium also had the lowest copper concentration.

TABLE V. Occurrence of Cadmium in Marine Animals

Organism		Cd $\mu g/g$	*Concentration factor* $\times 10^{-3}$*
Protozoa			
Ramulina sp. (Foraminifera)†		2.18 2.24	19.5
Porifera			
Halichondria panicea		1.85	16.4
Coelenterata			
Alcyonium digitatum		1.15	10.2
Crustacea			
Balanus balanoides (Cirripedia)		0.146 0.148	1.30
Cancer pagurus (Decapoda)		0.153	1.35
Corystes cassivelaunus (Decapoda)		0.149	1.31
Eupagurus sp. (Decapoda)		1.31	11.6
Mollusca			
Mytilus edulis (Lamellibranchia)	Shell only	0.003	0.03
	Soft parts	3.21	28.4
Pecten maximus (Lamellibranchia)			See Table IX
Chlamys opercularis (Lamellibranchia)			See Table VII
Littorina littoralis (Gastropoda)		3.54	31.3
L. littorea (Gastropoda)	Shell only	0.012	0.1
	Soft parts	1.84	16.3
Nucella lapillus (Gastropoda)	Shell only	0.082	0.72
	Soft parts	37.9	335
Calliostoma zizyphinum (Gastropoda)	Shell only	0.049	0.43
	Soft parts	3.05	27.0
Gibbula umbilicalis (Gastropoda)	Shell only	0.029	0.26
	Soft parts	0.829	7.3
Patella vulgata (Gastropoda)		16.4	145
Buccinum undatum (Gastropoda)			See Table VIII
Echinodermata			
Asterias rubens (Asteroidea)		1.66	14.7
Henricia sanguinolenta (Asteroidea)		1.12	9.6
Luidia ciliaris (Asteroidea)		14.8	131
Marthasterias glacialis (Asteroidea)		1.46	12.9
Porania pulvillus (Asteroidea)			See Table VI
Stichastrella rosea (Asteroidea)		6.3	56.1
Echinus esculentus (Echinoidea)		0.325	2.8
Psammechinus miliaris (Echinoidea)		0.435 0.450	3.8
Spatangus purpureus (Echinoidea)	Whole organism less gut	0.24	2.1
	Gut & contents	0.81	7.2
Ophiocomina nigra (Ophiuroidea)		0.940 0.963	8.1

† From Galle, Ceylon.

* Concentration factor = concentration of cadmium in air-dried organism/mean concentration of cadmium in seawater (0.113 $\mu g/l$).

These values are calculated from the mean value in the preceding column.

TABLE VI. CADMIUM IN *Chlamys opercularis*

	Shell	*Gills*	*Mantle + Viscera*	*Muscle*	*Gonad*
Sulphated ash, %	—	19.0	21.6	6.5	10.4
Cd, μg/g	0.008	1.24	9.71, 9.53*	0.87	2.21
Conc^{n}. factor × 10^{-3}	0.007	11	85	8	20
Cd in ash, μg/g	0.008	6.5	44.5	13.4	21.2

* Duplicate determinations on different samples.

TABLE VII. CADMIUM IN *Porania pulvillus*

	Inter-radial septa	*Skin from aboral surface*	*Ambulacral region + Tubefoot system*	*Oral region + Stomach*	*Digestive gland*	*Gonad*
Sulphated ash, %	73.7	60.4	88.3	95.0	11.3	—
Cd, μg/g	13.1	16.3	6.8	6.7	2.23	1.47
Conc^{n}. factor × 10^{-3}	115	144	60	59	20	13
Cd in ash, μg/g	17.7	26.9	7.7	7.0	19.7	—

Marine organisms. Cadmium has been determined in a number of species of marine algae and marine animals, obtained mainly from the Irish Sea, off Port Erin and Port St. Mary. The organisms were washed thoroughly with distilled water and dried at 110° before analysis. Unless otherwise noted, the analyses were carried out on the whole organism. Duplicate analyses, carried out in a number of cases, showed excellent agreement. In addition, the distribution of cadmium in the various organs of *Porania pulvillus*, *Chlamys opercularis*, *Buccinum undatum*, and *Pecten maximus* has been studied. Specimens of *Pecten maximus* were analysed directly after removal from their habitat and also after being allowed to purge themselves in clean seawater for seven days. The results of the analyses are shown in Tables IV–IX, together with the concentration factors [concentration of cadmium in dried organism (in μg/kg)/mean concentrations of cadmium in seawater (0.113 μg/l)].

The cadmium concentrations of the various whole organisms lie in the range 0.13 (*Laminaria digitata*) to 16.4 μg/g (*Patella vulgata*) and show that the element is strongly extracted from seawater by marine organisms. The values found for *Fucus serratus*, *Ascophyllum nodosum*, and *Asterias rubens* accord well with those found polarographically in these organisms by Malyuga (0.34, 0.29, and 1.1 μg/g respectively). The extremely low cadmium content of the calcareous shells suggests that the mechanism by which the calcium of seawater is converted into calcium carbonate in the shell is extremely selective

TABLE VIII. Cadmium in *Buccinum undatum*

	*Whole animal**	*Shell*	*Mantle*	*Foot*	*Heart*	*Digestive gland*	*Digestive tract*	*Mucous gland*	*Renal organ*
Sulphated ash, %	8.8	—	5.0	4.1	5.4	4.1	5.7	20.4	10.0
Cd, μg/g	31.8	0.018	0.96	0.29	2.32	68.0	3.14	1.31	17.7
Conc^{n}. factor $\times 10^{-3}$	281	0.16	8.5	2.6	21	602	28	12	157
Cd in ash, μg/g	361	0.018	19	7	43	1659	55	6	177

	Male ducts	*Female ducts*	*Male gonads*	*Female gonads*	*Operculum*	*Osphradium*	*Ctenidium*
Sulphated ash, %	5.9	3.3	—	2.1	3.7	4.0	10.9
Cd, μg/g	0.72	0.60	24.3	11.4	1.0	15.4	11.2
Conc^{n}. factor $\times 10^{-3}$	6.4	5.3	215	101	8.8	136	99
Cd in ash, μg/g	12	18	—	542	27	385	102

* Less shell.

TABLE IX. CADMIUM IN *Pecten maximus*

Unpurged

	Shell	*Gills*	*Full gonad*	*Spent gonad*	*Striped muscle*	*Unstriped muscle*	*Foot*
Sulphated ash, %	—	25.1	10.7	3.2	6.0	4.7	51.9
Cd, μg/g	0.001	8.5	0.79	9.3	1.95	1.86	6.3
Conc^{n}. factor × 10^{-3}	0.01	75	7	82	17	16	56
Cd in ash, μg/g	0.001	34	7.3	291	33	40	12

	Mantle + Gut + Digestive gland	*Mantle*	*Gut*	*Digestive gland*	*Renal organ*
Sulphated ash, %	13.9	13.3	12.6	7.2	27.2
Cd, μg/g	39.5	5.8	6.2	532	152
Conc^{n}. factor × 10^{-3}	350	49	55	4707	1348
Cd in ash, μg/g	284	44	49	7400	559

Purged

	Gills	*Male gonad*	*Female gonad*	*Striped muscle*	*Foot*	*Gut + Gonad + Digestive gland*	*Mantle*	*Renal organ*
Sulphated ash, %	25.0	3.0	10.2	12.7	9.3	10.9	9.4	36.7
Cd, μg/g	12.5	0.55	0.11	1.58	16.5	111	4.1	127
Conc^{n}. factor × 10^{-3}	111	45	1	14	146	983	36	1124
Cd in ash, μg/g	50	18	11	12	177	1018	44	346

TABLE X. Cadmium in Marine Sediments

Sample	Sea or Ocean	Lat.	Long.	Depth (m)	μg Cd/g	Concentration factor × 10^{-3}
Barbados earth[1]	—	—	—	—	0.023	0.20
Diatomaceous ooze	S. Atlantic	53° 35′ S	108° 35′ E	3566	0.857	7.6
Diatomaceous ooze[2]	—do—	66° 40.5′ S	71° 01′ W	531	0.281	2.5
Diatomaceous ooze[3]	—do—	54° 03′ S	38° 35′ W	184	0.174	1.5
Diatomaceous ooze[4]	—do—	62° 56′ S	59° 50′ W	949	0.311	2.8
Diatomaceous ooze[5]	—do—	55° 52′ S	56° 53′ W	4344	0.311	2.7
Globigerina ooze[6]	—do—	25° 30′ S	5° 53′ E	892	0.459	4.1
Globigerina ooze	N. Atlantic	38° 55.6′ N	31° 35.0′ W	1295	0.275	2.4
Globigerina ooze[7]	Atlantic	26° 07.7′ S	14° 36.3′ W	2260	0.516	4.6
Radiolarian ooze[8]	S. Pacific	11° 14′ S	97° 57′ E	5032	0.448	4.0
Radiolarian ooze[8]	N. Pacific	12° 42′ N	152° 01′ W	5300	0.251	2.2
Radiolarian ooze[9]	S. Atlantic	46° 35′ S	24° 15.5′ W	4402	0.129	1.1
Radiolarian ooze[10]	—do—	50° 26′ S	30° 27′ W	5000	0.977	8.6
Red clay[11]	Pacific	19° 10.2′ N	177° 24.1′ E	3566	0.563	5.0
Green mud	N. Atlantic	44° 37.6′ N	55° 47.1′ W	1049	0.268	2.3
Calcareous ooze[12]	—do—	22° 00.5′ N	76° 59.5′ W	914	0.574	5.1
Drewite[13]	Caribbean	24° 10′ N	78° 00′ W	—	0.124	1.1
Volcanic glass[14]	S. Atlantic	62° 59′ S	60° 28′ W	525	0.210	1.9
Nullipore gravel[15]	Atlantic	—	—	40	0.106	0.9
Manganese nodule[16]	N. Pacific	37° 41′ N	177° 04′ W	5303	8.40	74.3
Manganese nodule[17]	S. Pacific	13° 28′ S	149° 30′ W	4300	5.06	44.8
Organic mud[18]	Irish	54° 10′ N	4° 58′ W	66	0.075* 0.417†	0.7 3.7
Organic mud[19]	Irish	54° 24′ N	3° 34′ W	18	0.096* 0.363†	0.8 3.2

* Nitric acid soluble Cd.
† Total Cd.

for calcium (see p. 120). In general, the cadmium contents of algae and Asteroidea were higher than those of Crustacea although generally lower than those of Mollusca. It is not obvious why the cadmium concentrations of *Patella* and *Nucella* are so much greater than those of other molluscs; *Patella* is a browsing form which feeds upon the microscopic algal film covering rocks; *Nucella*, on the other hand, is carnivorous, its diet consisting mainly of *Balanus*, an organism with a low cadmium content; the related shallow water form, *Buccinum*, also has a high cadmium content (Table VIII). The cadmium content of the various organs differs widely, particularly low concentrations being found in muscle and gonads. The element is much concentrated in the digestive glands and renal organs of those molluscs whose individual organs have been examined, contents of up to 0.5% in the ash being recorded. In the case of *Pecten maximus* it was thought that the cadmium in the digestive gland might be associated with the detritus on which the animal feeds; this did not prove to be the case, since animals which had been allowed to purge themselves in filtered seawater until the gut was empty were still rich in cadmium in these organs (Table IX). Copper is much more uniformly distributed throughout the organs of *Buccinum* (26) than is cadmium; excluding the shell and foot, the Cu content ranges from 26 to 87 μg/g.

NOTES TO TABLE X

[1] Neritic fossil deposit, mainly Radiolarian, from Bisset Hill.
[2] "Discovery" St. W.S. 514. 11/2/30.
[3] "Discovery" St. W.S. 52. Organic debris with siliceous skeletons.
[4] "Discovery" St. No. 203. 5/4/27, Bransfield Strait, S. Shetlands.
[5] "Discovery" St. W.S. 468. 9/11/29.
[6] Chalky deposit.
[7] Globigerina and sponge spicules.
[8] Debris and sponge spicules.
[9] "Discovery" St. No. 10. 13/2/26.
[10] "Discovery" St. No. 11. 16/2/26.
[11] Mainly volcanic debris and some sponge spicules.
[12] British Museum sample B.M. 1955, 24.
[13] From Miler Creek, South Bight, Andros Islands, Bahamas. Aragonite mud with a few drifted shells.
[13] "Discovery" St. No. 172. 26/2/27. Off Deception Island, S. Shetlands.
[15] From West Hebrides.
[16] British Museum sample No. M 313. Contained 20.3% SiO_2.
[17] Contained 16.5% SiO_2.
[18] Contained 1.2% organic carbon.
[19] Contained 1.3% organic carbon.

Marine sediments. A number of representative marine sediments have been analysed (see Table X). The cadmium contents of all the deep sea sediments, except manganese nodules, lie between 0.2 and 1 μg/g. Furthermore, there is no significant difference between the cadmium contents of diatomaceous ooze, globigerina ooze and radiolarian ooze (means 0.39, 0.42, 0.45 μg/g respectively). The mean concentration found is similar to that quoted by Goldschmidt (4) for the upper lithosphere (0.5 μg/g).

Goldberg (29), who has found that a number of elements are concentrated in manganese nodules, has attributed this to the scavenging action of the electrically charged colloidal ferric and manganese oxides, which adsorb oppositely charged ions from seawater before they coalesce to form the nodules. Evidently this is the explanation of the comparatively high cadmium content of the nodules examined. In passing it might be added that both nodules contained appreciable amounts of thallium (*ca* 2 μg/g), an element which, as stated on p. 106, has not been detected previously in seawater.

The low cadmium contents of carbonate shells and of Barbados earth are noteworthy, since, as mentioned on p. 105, Goldschmidt considered that both cadmium and zinc should be concentrated in carbonate sediments. The chemically precipitated drewite, on the other hand, contains considerable amounts of cadmium, and in laboratory experiments we have found that aragonite, which has been precipitated by passing a current of carbon dioxide-free air through seawater saturated with calcium carbonate, contains up to 1 μg/g of cadmium. It is apparent, therefore, that considerable amounts of cadmium are coprecipitated with chemically precipitated calcium carbonate, whereas when the latter is formed biologically the mechanism of shell formation is much more specific for calcium, with only small amounts of cadmium being incorporated in the shells.

The mud samples examined are of interest since they indicate that part of their cadmium is associated with the organic detritus which is derived from dead organisms. Assuming that the concentration of undecayed organisms in the mud was approximately twice the organic carbon content found, then the concentration of cadmium in the original organism was *ca* 4 μg/g, which is of the same order as that actually found in marine organisms.

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THE LAMINARIACEAE OFF NORTH SHAPINSAY, ORKNEY ISLANDS; CHANGES FROM 1947 TO 1955

By

F. T. WALKER[1] AND W. D. RICHARDSON[2]

Institute of Seaweed Research, Musselburgh, Midlothian

ABSTRACT

Changes in the crops of Laminariaceae over a number of years around Scotland have been investigated. This paper summarises the results of five surveys carried out in 1947, 1951, 1952, 1953 and 1955 in North Shapinsay, Orkney Islands. Considerable losses were found between 1947 and 1952, but thereafter recovery commenced and has continued. Some of the ecological factors are analysed and discussed.

INTRODUCTION

During the last ten years, 1946 to 1955, an extensive survey of Laminariaceae around Scotland has been in continuous operation. The marine coast of Scotland and of its many islands, 6,700 miles in all, has been photographed through co-operation of the Royal Air Force. With the aid of these aerial stereoscopic photos and with ecological data obtained by methods of quadrat sampling of the seabed (Walker, 1947), it has been possible to assess the Laminariaceae growing around Scotland (Walker, 1954a).

Since 1946, 86 sublittoral surveys, carried out from chartered motor vessels, have been completed, and the data obtained have been statistically analysed. The areas surveyed thus far, totaling 67,000 acres (27,000 hectares), are located off the northeast, northwest, southeast and southwest mainland, off the Orkney Islands, and off the Isle of Skye. Resurveys of many of these areas revealed that considerable changes in abundance in a crop of Laminariaceae occurred over a number of the years.

Of the family Laminariaceae, two species predominated around Scotland: the perennial *Laminaria cloustoni* Edm. (*L. hyperborea* Fosl.) and the annual *L. saccharina* Lamour. While individual plants of *L. saccharina* can grow for two or three years, the majority stand little chance of survival from one year to another.

Part of this ecological programme consisted of surveys of (1) four habitats of *L. cloustoni* in widely separated areas—NE, SE, NE, NW

[1] Now with Dept. of Agriculture for Scotland.

[2] Now with Imperial College of Tropical Agriculture, B.W.I.

mainland of Scotland, and (2) two habitats of *L. saccharina*, one during summer, the other during winter. This paper records the results of five summer surveys of a crop of *L. saccharina* established over an area off Shapinsay, one of the Orkney Islands between the Scottish mainland and the Shetland Islands. Results of the winter surveys of *L. saccharina*, carried out off the Isle of Arran in the Firth of Clyde, have been presented elsewhere (Walker and Richardson, in press).

The survey area off Shapinsay lies between Galt Ness and Sandy Geo, including the extensive Veantrow Bay, North Shapinsay. The surface of the seabed in this area consists of rocks, boulders and sand. Old Red Sandstone is the characteristic geological formation of the Orkney Islands. The mean tidal range is one fathom (1.85 m), and during spring tides the rate of the tidal stream passing the north-west coast of Shapinsay reaches 6 to 7 knots.

The first of the five surveys, carried out in May 1947 before the "May cast," employed quadrat sampling at one-fathom depth intervals from one to six fathoms along transects measured by rangefinder: the transects were 200 yards (185 m) apart (Walker, 1950). The four subsequent surveys took place during July of 1951, 1952, 1953 and 1955 after the "May cast," when random sampling was pursued with an intensity of 250 quadrats per square kilometre between low water and ten fathoms (18.5 m).

Nearly 18,000 quadrats, using calibrated spring grabs, were sampled during these five surveys. All depths were measured to the nearest fathom and were standardised to low water mark at ordinary spring tides. Seaweed density quoted herein represents the mean fresh weight of algae per unit area. The algae were weighed on a spring balance to the nearest half-pound immediately upon being taken from the sea. Seaweed cover is indicated by the number of quadrats which contained Laminariaceae, expressed as a percentage of all quadrats.

During the month of May the lamina (or frond) of the perennial *L. cloustoni* is shed after a new lamina has been partially produced by intercalary growth between the stipe and the mature lamina that was produced in the previous year. The shedding of the old lamina is known as the "May cast," much of which is cast up on the beach though some is carried out to greater depths. Shedding of the old lamina reduces considerably not only the plant weight but the total crop as well. Also, winter storms disrupt the balance of the crop by tearing off larger plants from the seabed; these also may be cast up on beaches or carried out to greater depths.

Reproduction of *L. saccharina* occurs in September and of *L. cloustoni* in December, so that by the early part of the year large numbers of small plants are recolonising any suitable and available area of the seabed. Only a small percentage reach maturity.

The Laminariaceae undergo an alternation of generations; zoospores give rise to a heteromorphic generation of microscopic filamentous gametophytes whose ova and sperm on fertilisation grow into macroscopic sporophytes (Walker, 1954b).

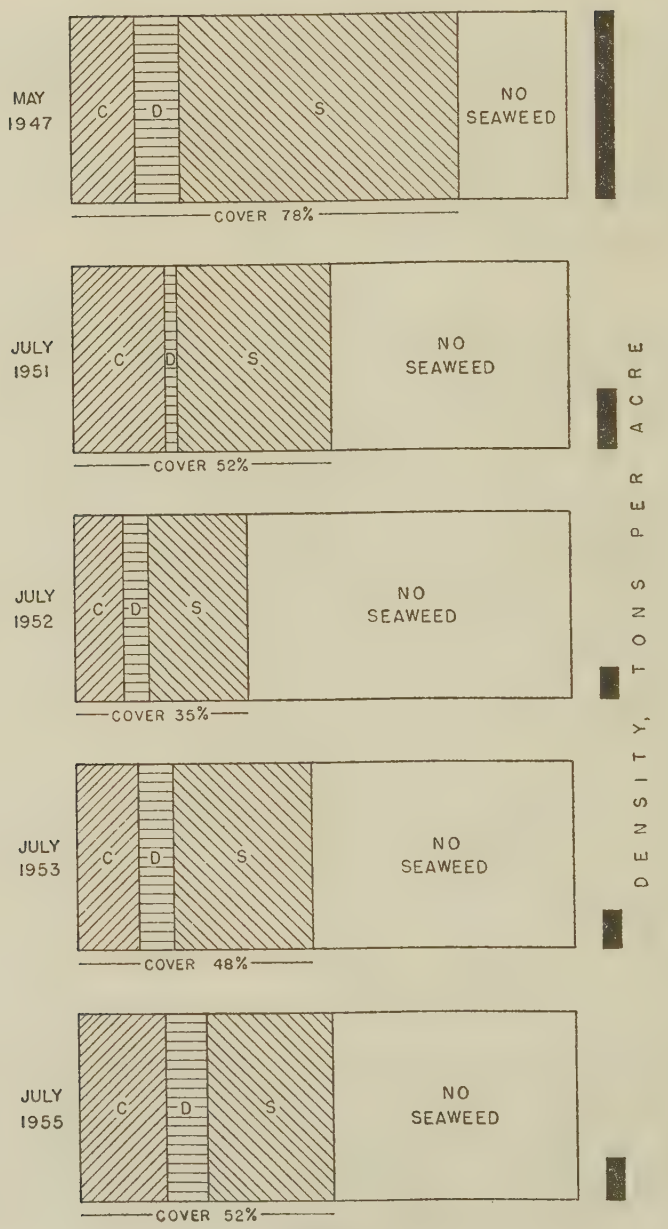
RESULTS

The calculated totals of Laminariaceae, covering 1,040 acres of the sublittoral zone between one and six fathoms for the five surveys, are given in Table I, together with corresponding density and cover. Although samplings in 1951, 1952, 1953 and 1955 were taken to a depth of 10 fathoms, the values in Table I are restricted to a range from one to six fathoms, which were the limits set by economic considerations in the earlier years of the research programme. The standard errors of mean density are calculated by the method of pooled variances for individual depths, based on unit quadrats of one square yard. The sampling was sufficient to cope consistently with the variations within the algal crop of this area. The cover with ratio of species (based on relative fresh weight) and the density are shown diagrammatically in Fig. 1.

TABLE I

Date	*Total seaweed; fresh weight (tons)*	*Seaweed cover (%)*	*Mean density; fresh weight (ton/acre)*	*Standard error of mean density (%)*
May 1947	33,960	78	32.6	—
July 1951	9,890	52	9.5	2
July 1952	5,830	35	5.6	3
July 1953	6,860	48	6.6	3
July 1955	7,590	52	7.3	3

Cover decreased during the four year interval from 1947 to 1951 and still further from 1951 to 1952; but by 1953 it had increased and continued to do so until the observations were terminated in 1955. *L. saccharina* accounted for most of the change. From 1951 to 1955, changes in the species ratio were more conspicuous in deeper water, where *L. saccharina* gave place to *L. cloustoni;* in shallower water, *L. cloustoni* gave place to *L. digitata* (Fig. 2).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D
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SEAWEED
COVER 78%
JULY
1951
C
D
S
NO
SEAWEED
COVER 52%
JULY
1952
C
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S
NO
SEAWEED
COVER 35%
JULY
1953
C
D
S
NO
SEAWEED
COVER 48%
JULY
1955
C
D
S
NO
SEAWEED
COVER 52%
DENSITY, TONS PER ACRE

Figure 1

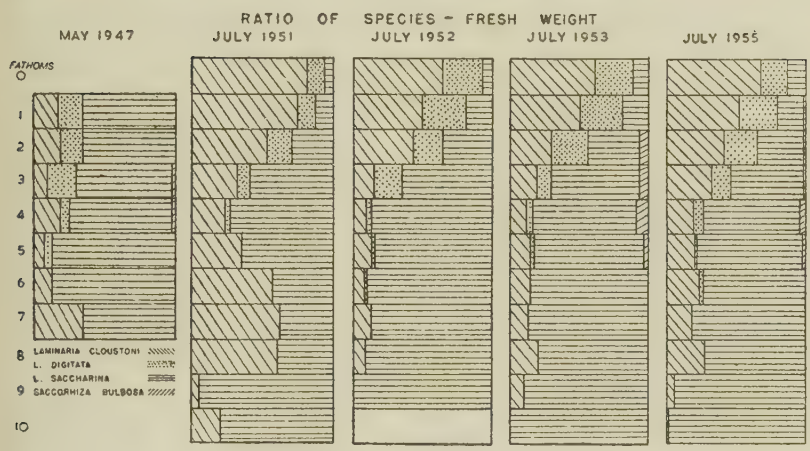


Figure 2

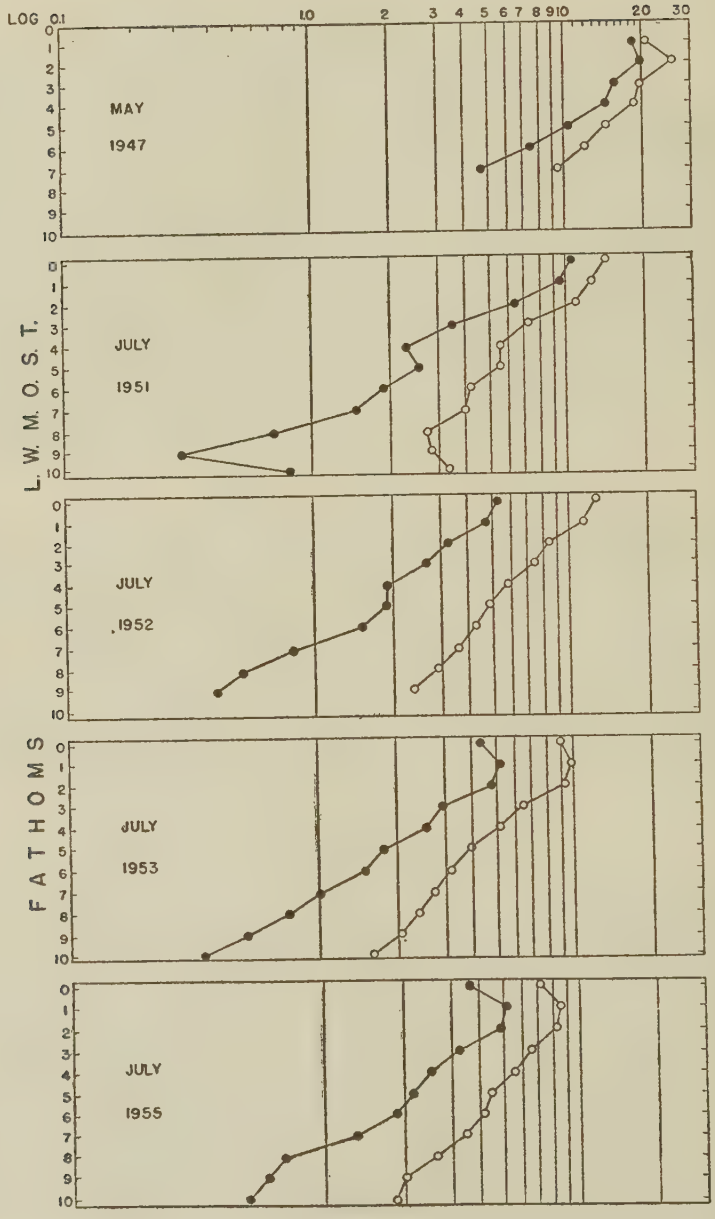
Fig. 3 gives plots of the mean values of seaweed density (on $\log^{10}$ scale) of Laminariaceae against fathom intervals of depths, calculated from all quadrats and from only those quadrats containing Laminariaceae. There is fair approximation to straight-line log regression with increasing depth, as might be expected where photosynthesis occurs with light transmitted through water.

It has been found that there is a relationship between density, cover and depth at which the Laminariaceae grow around Scotland (Walker, 1950, 1954a). This relationship may be expressed as follows:

$$\sqrt{\frac{d}{C}} = k - \gamma f \quad ,$$

where d is mean density based on total quadrats for a particular depth (lb/sq yd), C the corresponding cover (%), k a constant for the survey, γ the coefficient of regression, and f the depth in fathoms. The values for $\sqrt{d/c}$ for the five surveys, over a range from 1 to 6 fathoms, are plotted in Fig. 4. The movement of the graphs is not progressive with time; this would be unlikely, since the area must be recolonised by young plants after any violent disruption of the crop.

It is possible to recognise three fairly distinct phases (listed below), each of which is directly influenced by (a) the number of plants per unit area, (b) the mean weight per plant, and (c) the algal cover of an area. The product of these three factors gives the total weight of the crop.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30
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1947
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JULY
1955
L. W. M. O. S. T.
FATHOMS

Figure 3

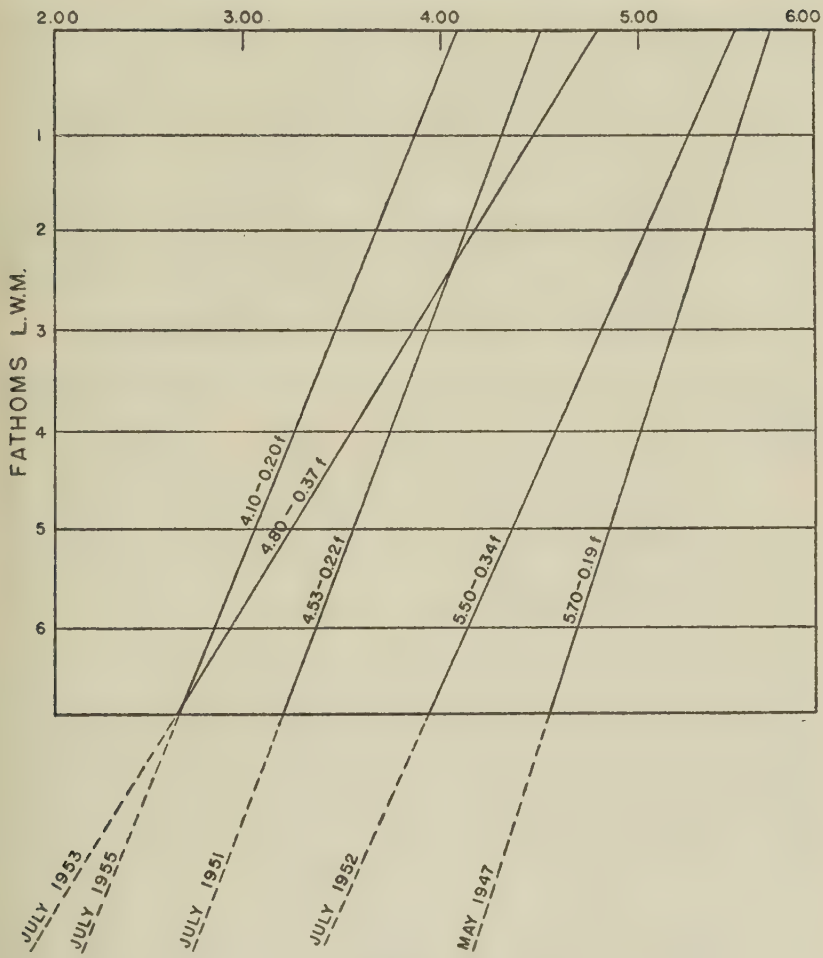

Figure 4

1. *A destructive phase* is marked by a decrease in the population, as for example after 'strong gales,' when large quantities of seaweed are cast.

(a) The number of plants decreases.
(b) The *mean* weight per plant decreases because the larger plants are most vulnerable during strong gales.
(c) The cover decreases.

2. *A colonization phase*, when algae are recolonising an area and the population is increasing.

(a) The number of plants increases as new young plants begin to establish themselves in areas previously cleared of plants during a 'destructive phase.'
(b) The mean weight per plant decreases initially, since the addition of young plants brings down the value; with the addition of only relatively few young plants the value may remain unchanged or it may show small increases by increments of growth of the mature plants.
(c) The cover increases as new areas are colonised.

3. *A growth phase*, when populations of newly established algae are maturing.

(a) The number of plants may remain unchanged, but ultimately a decrease will occur as the plants compete for light and space.
(b) The mean weight per plant increases as young plants approach maturity.
(c) The cover continues to increase.

Ultimately, a crop will attain maximum density and cover which a particular habitat can support, but in nature the maxima may be reached only after the crop has been subjected to a series of 'destructive phases,' which these ecological researches show are seasonal (Walker and Richardson, 1955) and perennial (Walker, 1954a). If this scheme is applied to the data obtained in four of these surveys (July 1951, 1952, 1953 and 1955), then it appears that a 'destructive phase' occurred between 1951 and 1952 and 'colonisation phases' between 1952 and 1955.

For 1952, 1953 and 1955, the number of plants and their mean weight are given in Table II. In the case of *L. saccharina*, the predominant species, the number of plants increased as the mean weight per plant decreased, indicating a period of recolonisation from 1952 to 1955. Only those quadrats which contained a single species of *Laminaria* (75%) were used to compile this table.

The coefficient of variability is a useful statistic for comparing the behaviour of a crop growing under a complex set of ecological factors, each subject to change. Such coefficients for the 1951, 1952, 1953 and 1955 surveys are shown in Fig. 5.

It will be seen that the 'outsiders' occur in 1951 and 1955. During

TABLE II. Mean Number of Plants per Square Yard and Mean Fresh Weight per Plant (without Holdfast) of the Chief Species of Laminariaceae Found at Various Depths

Species	*Depth (fathoms)* L.W.M.O.S.T.	*Mean number of plants per sq yd* 1952	1953	1955	*Mean weight per plant (lb)* 1952	1953	1955
Laminaria cloustoni	0	6.1	7.1	6.1	2.2	1.2	1.2
	1	5.6	7.6	8.0	2.0	1.2	1.3
	2	4.6	10.6	9.1	2.5	1.0	1.4
	3	5.3	7.9	8.2	2.3	1.3	1.3
	0–3 as a whole	5.5	8.1	7.5	2.2	1.1	1.3
Laminaria digitata	0	4.0	5.0	5.1	2.3	1.1	1.0
	1	4.9	4.9	4.5	2.1	2.0	1.5
	2	6.0	5.4	7.1	1.8	2.1	1.6
	3	7.3	5.3	2.0	2.0	2.7	1.0
	0–3 as a whole	5.5	5.1	5.8	2.0	1.9	1.4
Laminaria saccharina	0	8.0	4.9	6.2	1.0	0.6	0.5
	1	7.8	5.0	6.9	1.0	0.6	0.4
	2	4.8	6.7	7.6	1.0	0.7	0.6
	3	6.3	7.5	7.2	0.9	0.6	0.6
	4	6.5	6.8	7.4	0.8	0.6	0.6
	5	5.6	6.3	7.0	0.8	0.5	0.5
	6	4.9	5.7	6.6	0.8	0.5	0.5
	7	3.8	4.7	5.6	0.8	0.5	0.6
	8	3.3	4.2	5.1	0.8	0.5	0.4
	9	2.9	4.1	4.6	0.8	0.5	0.4
	10	—	3.5	4.1	—	0.6	0.5
	0–9 as a whole	5.3	5.9	6.7	0.8	0.6	0.5

1951, when the crop was declining, these coefficients were of less value, whereas during 1955, when the crop was recovering, they were of greater value. A declining laminarian crop also loses its variability while a recolonising crop gains variability as more generations appear. These crop changes fit into the ecological pattern found around Scotland during the last ten years, the general trend of which indicates an eleven-year cycle with logarithmic annual change; this cycle coincides with that of the sun-spot activity (Walker, 1956).

The seaweed cover of the above surveys and the incidence of strong gales in the Orkney-Shetland area have been found to be related mathematically; this may serve as a pointer in future research.

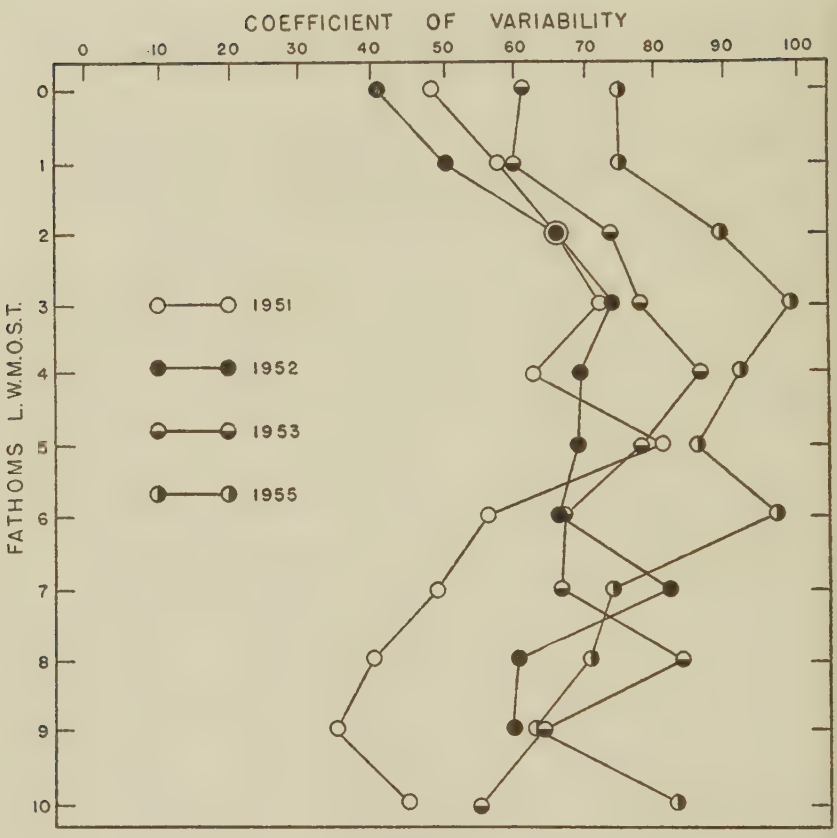

Figure 5

ACKNOWLEDGMENTS

These ecological surveys are part of the programme of research at the Institute of Seaweed Research, and we appreciate the Director's permission to publish these results. We also thank members of the Scientific Advisory Committee of the Institute, under the Chairmanship of Professor E. L. Hirst, F.R.S., and of the Algological Advisory Committee, under the Chairmanship of Sir William Wright Smith, F.R.S., as well as Professor T. A. Bennet-Clark, F.R.S., for their constructive criticism.

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THE PROCESSES OF SOUND SCATTERING AT THE OCEAN SURFACE AND BOTTOM

By

R. J. URICK

Ordnance Research Laboratory
The Pennsylvania State University
University Park, Pennsylvania

ABSTRACT

In order to have a firm basis for the prediction of reverberation or back-scattering of sound in the sea, field measurements leading to values for a back-scattering coefficient of the sea surface and bottom have been made. Variation of this coefficient with angle of incidence of the sound beam provides some interesting clues as to the back-scattering processes which operate. It is suggested that three different processes of scattering from the sea surface are dominant in different ranges of angle between grazing and normal incidence. At angles near normal incidence, sound appears to be returned toward the source by mirror-like reflection from wave facets. At angles near grazing incidence, a scattering layer below the surface is indicated as the important scatterer at moderate sea states. At intermediate angles, rough-surface scattering by small surface irregularities is suggested as the dominant source of scattering. For bottom-scattering, the latter process appears to be the important one at all angles of incidence for the harder bottom types.

INTRODUCTION

At present there are numerous applications of underwater sound, mostly in connection with naval warfare where its military use lies in submarine detection, underwater communication, torpedo homing, and others. In civilian fields, underwater sound has more familiar uses in fathometry and fish-finding. In most of these practical applications, the boundaries of the sea—its surface and bottom—play an important part in the propagation of acoustic energy by confining and dispersing sound that impinges upon them.

If these boundaries were ideal plane surfaces, they would act like mirrors, merely reflecting any incident sound energy into the specular angle and producing no redistribution of energy other than this single change of direction. But these surfaces are rough, and in addition they appear to have other peculiar characteristics as acoustic boundaries. Because of this, they "back-scatter" or return incident sound toward the source, thereby giving rise, in the aggregate, to the "rever-

beration" which is so troublesome whenever echo-ranging on an underwater object is attempted.

The Ordnance Research Laboratory of the Pennsylvania State University has recently made measurements of acoustic back-scattering by the sea surface and bottom at various locations near Key West, Florida and Newport, Rhode Island. The primary aim of the work was to investigate the back-scattering coefficient as a function of angle, sea state, bottom type, and other variables in order to obtain a rational basis for the prediction of reverberation levels. As a by-product, the measurements appear to provide some (by no means conclusive) evidence of the processes by which sound is reflected and scattered by the ocean boundaries. This paper presents some conjectures regarding scattering phenomena which these measurements appear to make reasonable.

Since the angle of incidence of the sound beam was of prime importance as a determinant of scattering, the measurements have been principally concerned with the variation of scattering with angle. Two transducers—one used as a sound source, the other as a receiver—were mounted on a cylinder which could be rotated in a vertical plane so that the transducers, each having a beamwidth[1] of 14°, could be pointed at any desired angle toward the surface or bottom. A photograph of the cylinder and its associated handling gear on board a YF-Type vessel is shown in Fig. 1. With this equipment over the ship's side, a sound pulse of short duration was emitted by the sending transducer; the back-scattered pulse, returned by the surface or bottom, was received by the receiving transducer. The received pulse was amplified and photographed on the face of an oscilloscope screen. Some examples of the appearance of the back-scattered pulse are shown in Figs. 2–4. Suitable techniques for calibrating the equipment were employed so that the measured intensity of the back-scattering could be expressed as a certain ratio of the intensity of the emitted pulse at a unit distance.

Once this ratio has been obtained, it becomes a matter of geometry (by no means a simple one) to express the result in terms of a scattering coefficient of a unit area of surface and bottom. A number of different coefficients may be used to express the scattering or reflecting ability of a surface. The one that has been adopted in the present study has been called the *scattering strength* of unit area, in analogy with the similar unit, *target strength*, which denotes the corresponding

[1] Angle between points 3 db down on the transmitting or receiving beam pattern. For two-way transmission (transmitting and receiving) the corresponding angle is 7 degrees.

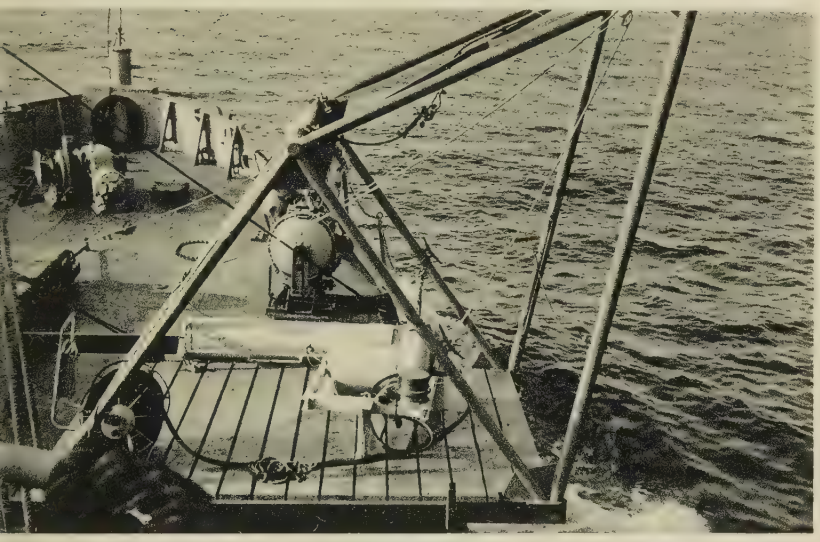
property of underwater objects. Scattering strength, which is related by a factor of 4π to the scattering cross-section of unit area, is the ratio of the scattered intensity from the unit area, measured at unit distance, to the intensity of the incident sound beam. Following naval practice, these distances are expressed in yards.

BACK-SCATTERING PROCESSES

The variation of this coefficient with angle provides some important clues to the scattering processes that operate. In Fig. 5 the pair of curves, together with the data points from which they were drawn, show scattering strength plotted vs. grazing angle (angle between the axial sound ray of the transducer beam and the horizontal) for surface scattering for two sea roughnesses when the wind speed was 5–9 knots and 13–18 knots, respectively. From this sample of a large amount of data it is seen that the scattering strength rises with increasing grazing angle, though the rate of rise is less in the case of rougher seas. As the surface becomes rougher, the scattering increases at the smaller angles and decreases at angles near normal incidence (90°). For both calm and rough seas at small grazing angles, the scattering strength is nearly independent of angle. This is not entirely clear in Fig. 5; but from other unpublished data obtained by the U. S. Navy Ordnance Test Station and by the Applied Physics Laboratory, University of Washington, it has been found that the surface scattering coefficient appears to be independent of angle from 2° to about 30°.

The corresponding curves for bottom scattering appear to be somewhat different. Fig. 6 shows the scattering curves obtained for four different types of bottom. These curves are more like the rough sea surface curves in that they do not show a sharp increase near normal incidence. Other data extending to smaller angles (1) show no tendency for bottom scattering strength to be independent of angle at low angles. In fact, the scattering from hard rocky bottoms appears to be more like that which would be expected for the return from a diffuse rough surface, which scatters light according to Lambert's "Law" (scattering strength proportional to the square of the sine of the grazing angle) (2).

Rather than give additional examples of observed surface scattering curves, three composite or typical curves, obtained by averaging and smoothing much reduced field data taken under a wide variety of conditions, are given in Fig. 7. The three wind speeds selected for these smoothed "typical" curves are 5, 10, and 15 knots. Considerable deviation, of the order of 2 to 5 db, from these average curves can be



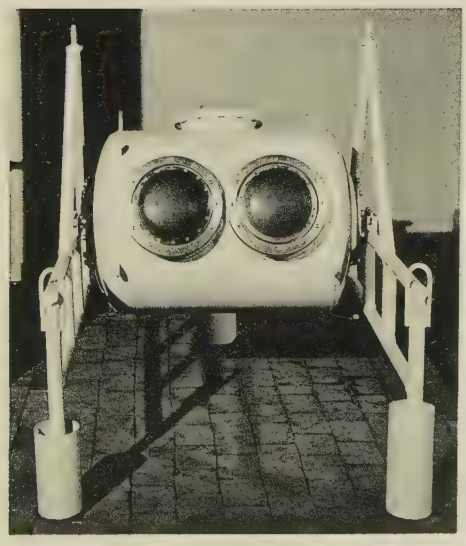


Figure 1. Photographs of the two-transducer rotatable cylinder used for back-scattering measurements.

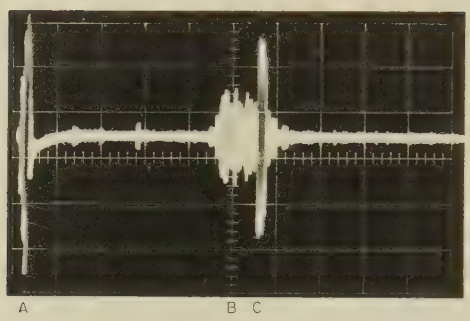


Figure 2. Photograph of a 0.5 ms pulse scattered back from the surface at normal incidence when the wind speed was 15 knots. Depth of the cylinder, 138 feet. Horizontal time scale, 10 milliseconds per division. *A,* initial pulse; *B,* return from subsurface layer; *C,* principal return from surface. The vertical scale is such that the return from the subsurface layer is 19 db below the principal surface-scattered pulse.

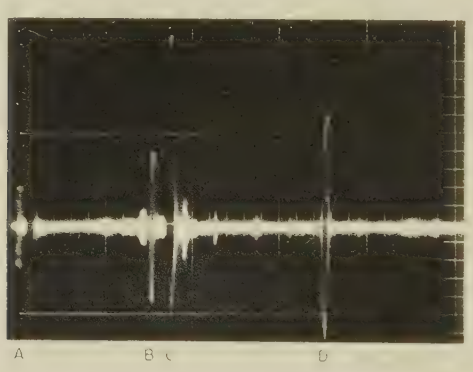


Figure 3. Photograph of a 0.5 ms pulse scattered back from the surface at normal incidence when the wind speed was 8 knots. Depth of cylinder, 40 feet. Horizontal time scale, 10 milliseconds per division. *A,* initial pulse; *B,* reflection from base of float suspending cylinder; *C,* principal surface return; *D,* a second reflection from cylinder and surface.

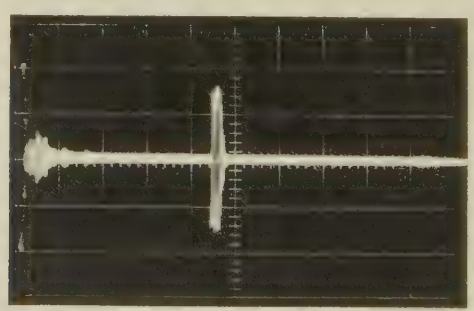


Figure 4. Photograph of a 5.0 ms pulse scattered back from the bottom in 580 feet of water. Bottom type, coral sand and rock. Horizontal time scale, 50 milliseconds per division.

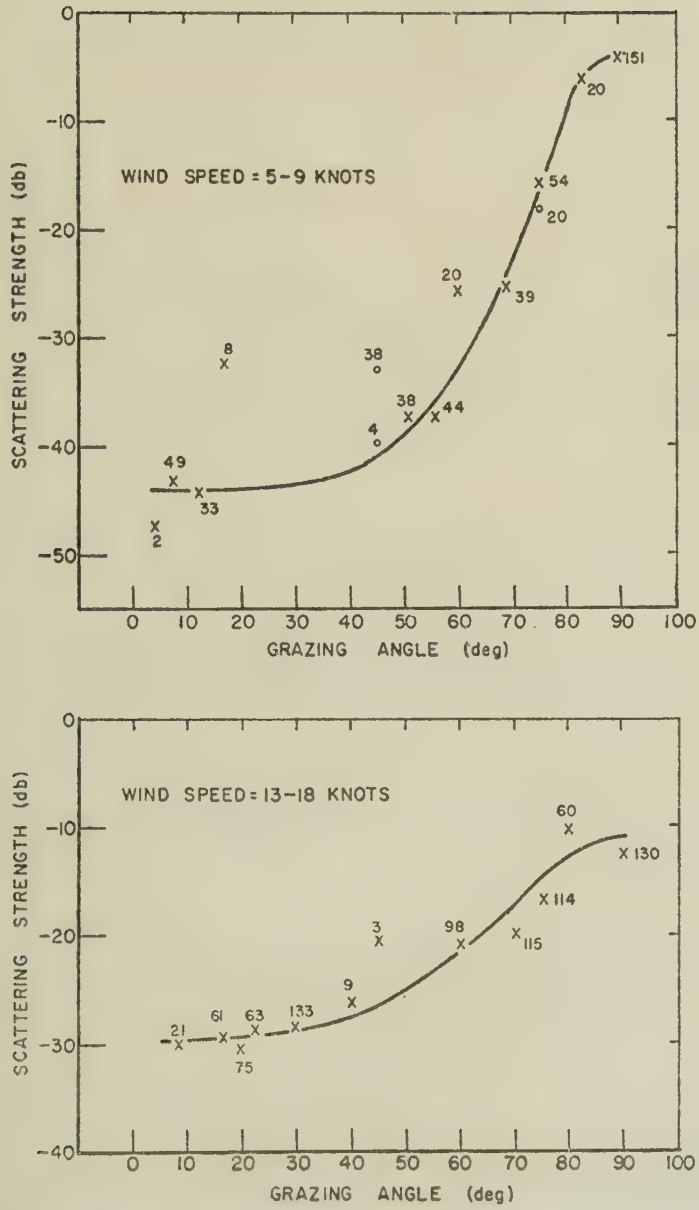


Figure 5. Observed surface scattering strength as a function of angle for two wind speeds. The numbers show the number of pulses averaged for each plotted point.

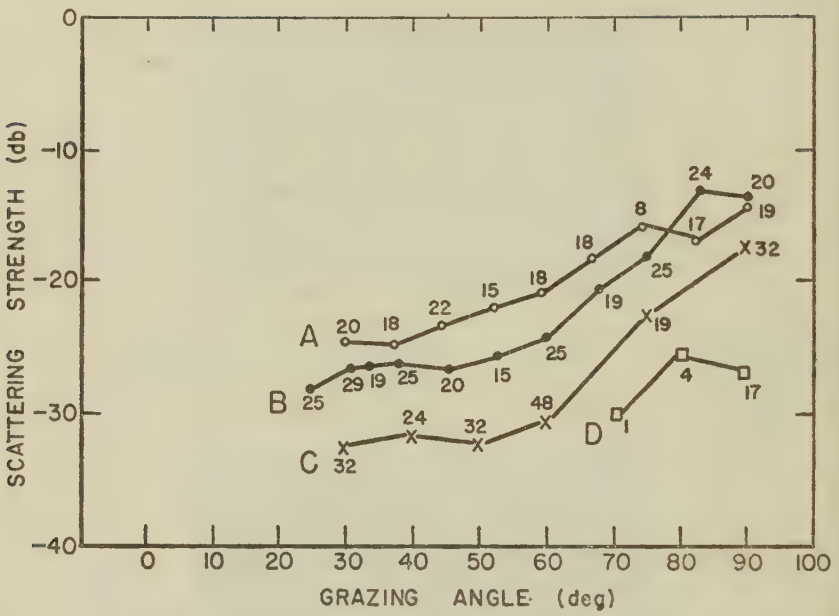


Figure 6. Observed bottom scattering strength as a function of angle for several types of bottom. The numbers show the number of pulses averaged for each plotted point. Bottom types as determined by bottom samples and chart location: *A*, *C*, Undifferentiated coral mud and rock off Key West, Florida; *B*, Mud and fine sand with shell near Newport, Rhode Island; *D*, Mud, deep water off Key West, Florida.

expected in mean measurements made at a particular time and place, and an even greater deviation exists for the scattering indicated by a single pulse; nevertheless, it is believed that these curves have meaning in showing the order of magnitude of scattering strength and its variation with angle.

For further discussion of these curves, we may divide the angular range from grazing to normal incidence into three regions, in each of which the dominant scattering process seems to be different. These three ranges, indicated in Fig. 7 as Regions I, II, and III, correspond roughly to the angular intervals 0°–30°, 30°–60°, and 60°–90°, respectively.

In Region I, the scattering in the rougher seas is sensibly independent of angle, at least down to about 2°, the lower limit to which existing data extend. This is a peculiarity that is difficult to reconcile with any scattering process involving the surface alone, since scattering by surface roughnesses (comparable with or smaller than a wavelength) would be expected to show an appreciable variation with angle near

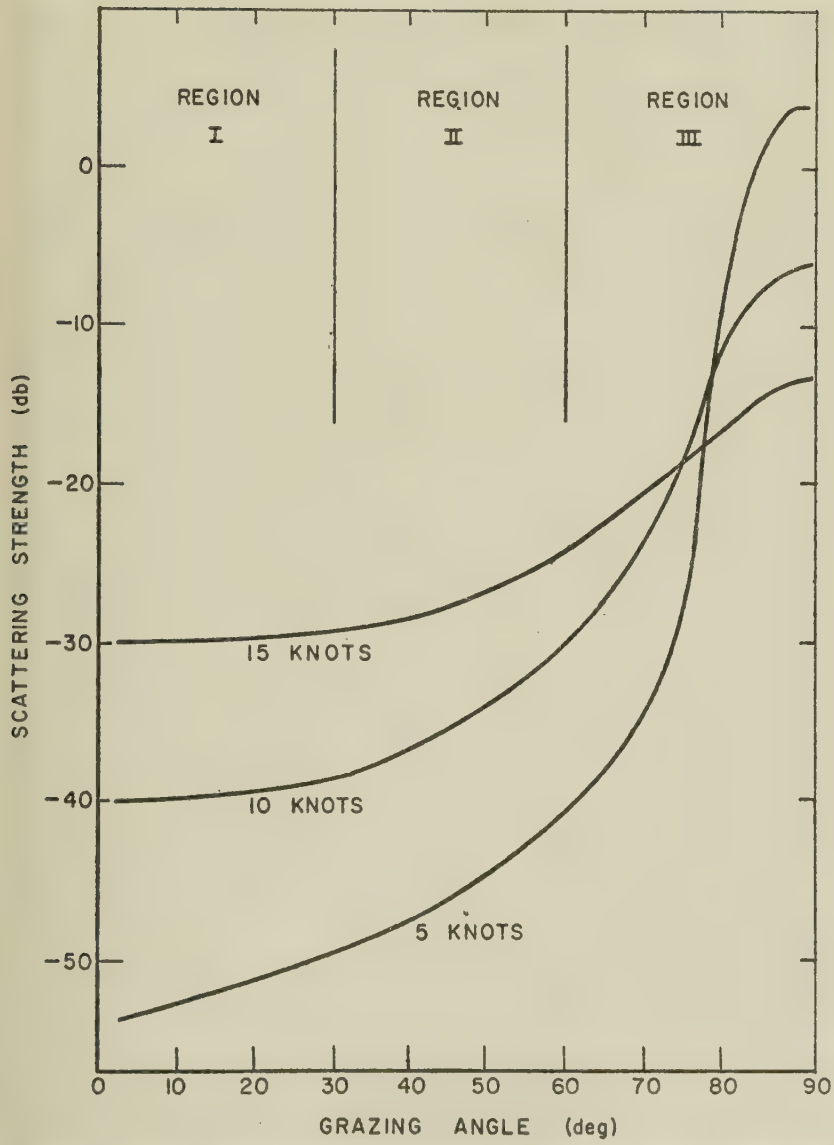


Figure 7. Smooth curves of surface scattering strength obtained by averaging field data. Estimated mean deviation of a data point (such as those plotted in Fig. 2) from these curves, 3 db. In the three regions it is suggested that the scattering processes are different.

grazing incidence. The usual behavior of rough-surface scattering (summarized by Lambert's Law), the shadowing of waves by intervening troughs, and the reduction of sound level at small angles by the pressure-release effect of the surface, would all conspire to give a variation with angle expressed by some high power of angle, probably of the order of 3 or 4.

In order to explain the observed isotropic scattering, imagine a scattering layer that is located near the surface and that is several wavelengths or more in thickness. Such a layer has been postulated before (3) as a possible source of surface scattering, even though no direct evidence for its existence appears to have been published. The most likely content of this layer is air bubbles whipped into the near-surface water by wind action. For some reason that is still a mystery, air bubbles are known to have an exceptionally long persistence in sea water (4). However, other forms of scatterers are possible, such as a layer of plankton. If it is assumed that air (or gas) bubbles of resonant size are responsible for a large part of the observed scattering, then a simple calculation indicates that at kilocycle frequencies a resonant bubble density of only 15 bubbles per cubic yard in a layer 3 yards thick is required to produce the scattering strength of -30 db indicated in Fig. 7 for a wind speed of 15 knots.

Some direct evidence for a near-surface layer is given by photographs of the return from the surface at normal incidence. With the transducers facing 90° upward, many oscilloscope traces show, at high wind speeds, a return arriving *ahead* of the main surface reflected pulse. In Fig. 2, a scattering layer some 25 feet in thickness appears to lie just below the surface. The magnitude of the scattering strength corresponding to the amplitude of the presurface return agrees roughly with the scattering strength found at low grazing angles. There is no indication of a scattering layer either below the surface at low wind speeds (Fig. 3), or above the bottom (Fig. 4).

Turning next to Region III, near normal incidence (Fig. 7), the slope of the curves in this region and their behavior with surface roughness suggest that sound is returned by reflection (rather than scattering), probably by small flat wave-facets oriented normal to the incident sound beam. The reflection of light by such facets has been studied by measurements of the glitter pattern of the sun (5), (6), (7) and by measurements of the angular distribution of the surface-reflection of an overhead source of light (8). These optical studies have provided data on the statistical distribution of sea-surface slopes. In one extensive series (6) it was found that slopes of wave

facets large enough to reflect light were normally distributed in angle with a standard deviation of slope given by

$$\sigma^2 = .003 + 5.12 + 10^{-3} W \pm .004 \quad ,$$

where σ is the root-mean-square sea surface slope and W is the wind-speed in meters per second.

The principal question is whether the facets that reflect light from above are effective as reflectors of sound (with a much larger wavelength) from below. Such facets have been postulated (9) as being responsible for the reflection of radar waves having wavelengths between 1 and 10 cm, of the same order of magnitude as the sound waves of the present study. Evidence that somewhat similar facets reflect sound near normal incidence is given by the fact that the curves of scattering strength, S, in this region are sensibly portions of normal or Gaussian curves having a standard deviation about the same as what would be predicted from the results of optical measurements. If increasing roughness merely increases the inclination of the facets without affecting their size or number per unit area, then the area under these normal curves of scattering strength should be a constant (independent of wind speed, at least for low and moderate wind speeds) so that the total energy returned by the surface will remain the same. Fig. 8 shows three computed curves, expressed in db units, plotted against grazing angle for wind velocities of 4.8 and 12 knots, using standard deviations given by the formula quoted above. The similarity to the observed curves in Fig. 7 for Region III will be evident. Another comparison, showing more detail, is given in Fig. 9, where the mean observed values of scattering strength at 60°, 75°, and 90° on five days when the wind velocities were 12.9, 10, 6, and 10.5 knots are compared with a normal curve adjusted so that it passes through the observed value of S at 90° and has a standard deviation of 7°, corresponding to an 8 knot wind by the formula above. Also included in Fig. 9 is a curve showing the effect of the finite transducer beamwidth, again adjusted arbitrarily to pass through the observed point at 90°; this is the shape of the S-curve that would be obtained for a perfect mirror-like reflection as a result of the beamwidth of the transducers.

As the sea becomes rougher, the effectiveness of the specular return becomes less as the facets become smaller and as their inclination is increased by a higher wind speed. Above some wind speed, probably about 10 to 15 knots, any reflection from these facets becomes hidden by the scattering produced by the other processes. However, it should be mentioned here that essentially no rough-sea data (above 17 knots) have been obtained in the present experiments.

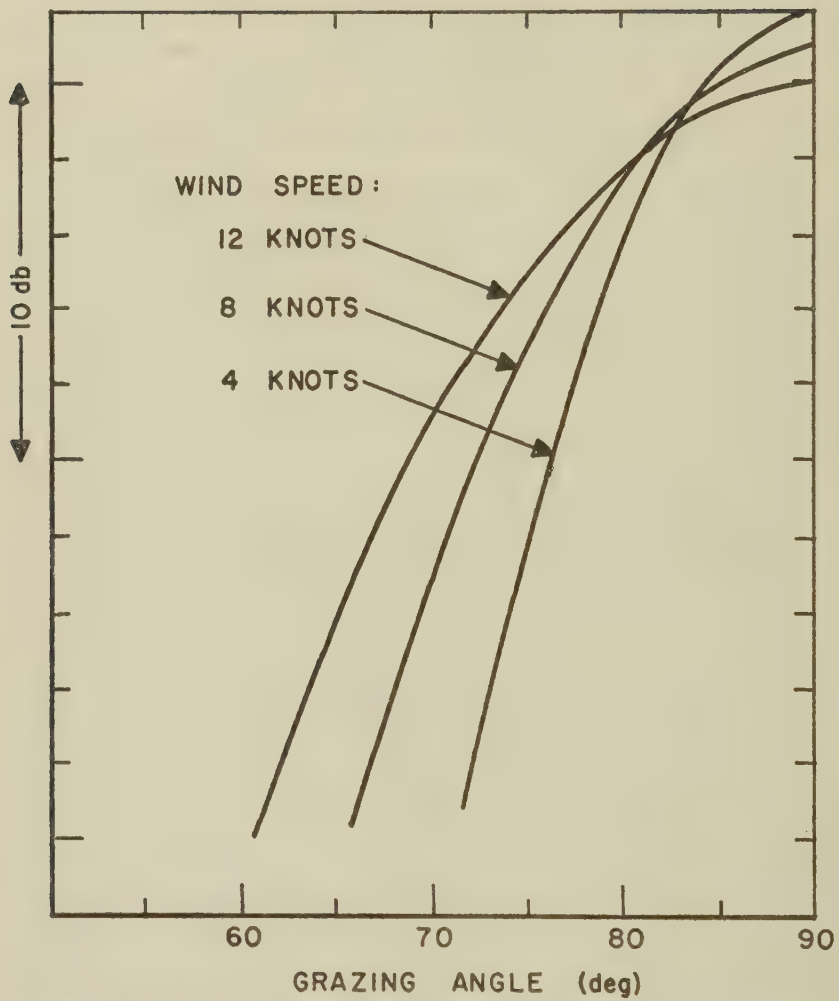


Figure 8. Normal curves of equal area having standard deviations according to the formula quoted in text, for the three wind speeds, 4, 8 and 12 knots.

It should be noted that the absence of a strong rise in the scattering curves for the bottom near normal incidence must mean that reflecting facets play no part in the return of sound from the bottom. Instead, it is likely that scattering by bottom roughness and irregularities is the dominant process at all angles of incidence, especially for the harder bottom types. For example, for two rocky bottoms examined

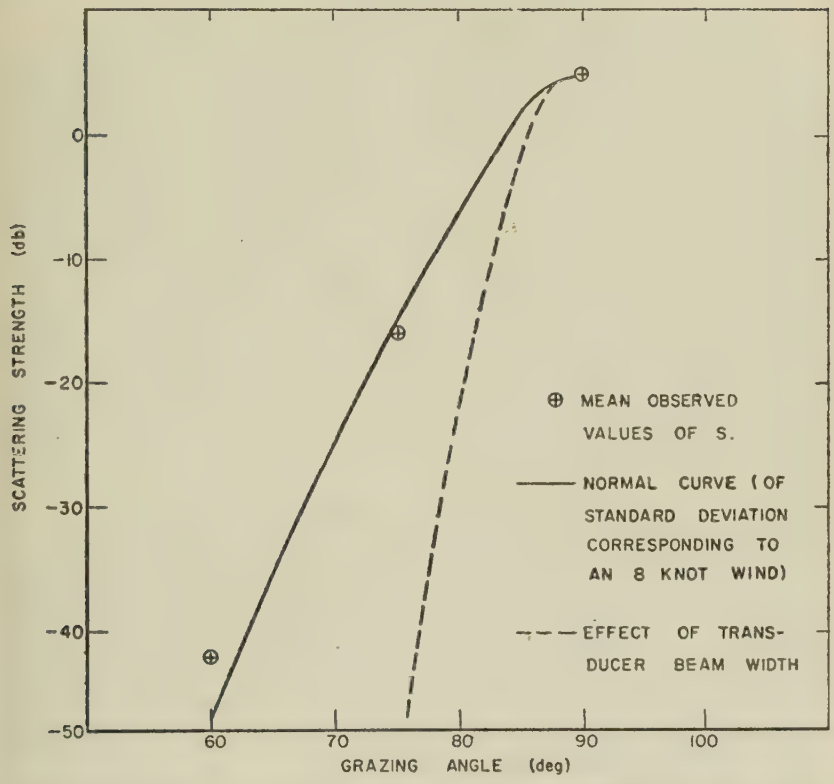


Figure 9. Comparison of mean S on five days for angles 60°, 75°, and 90° with the curve for an 8-knot wind speed (Fig. 8). The dotted curve would be obtained (with the transducers used) for a perfect mirror reflection. Both curves are adjusted to pass through the observed point at 90°.

in an earlier study (1), the curves of S were approximately like those of Lambert's Law over the range 10° to 90°, indicating that a hard bottom acts like a diffuse scatterer at kilocycle frequencies.

Turning finally to Region II of Fig. 7, it is tempting to speculate that the slow rise of S with angle in this region represents the effect of roughness scattering by surface irregularities that are much smaller than a wavelength. Small ripples and wavelets here may play their principal role as scatterers and cause a quasi-Lambert's Law behavior of scattering strength with angle. At large angles and in calm seas their effect is overwhelmed by reflection from wave facets; at low angles, where their scattering would drop off sharply with decreasing angle, their effect is submerged in the scattering from the subsurface layer.

SUMMARY

Data on the variation of back-scattering with angle has given some clues as to the processes by which the ocean surface and bottom scatter kilocycle-frequency sound in the backward direction. Three processes are suggested (Fig. 10). At low angles the data suggest that a scattering layer just below the surface, rather than at the surface itself, is the principal source of back-scattering so as to give rise to a scattering coefficient independent of grazing angle. At moderate angles, ripples and small wavelets may be the dominant scatterers and may give rise to a slow increase of scattering strength with increasing angle. At angles near normal incidence, specular reflection from wave facets appears to be the dominant process, except in rough seas where the facets become no longer effective as sound reflectors. Neither the first nor the third process appears to exist for scattering from the bottom which (at least for hard bottoms) seems to behave like a diffuse scatterer of sound.

ACKNOWLEDGEMENT

The work leading to these conclusions has been a co-operative endeavor by a number of members of the Ordnance Research Laboratory. W. L. Baker was largely responsible for the design and field operation of the equipment; D. T. Laird supplied an improved method of data analysis; and R. M. Hoover carried through the analysis of the field data and provided the curves and figures on which the conclusions are based. To all of these and others who participated in the work, the author is greatly indebted.

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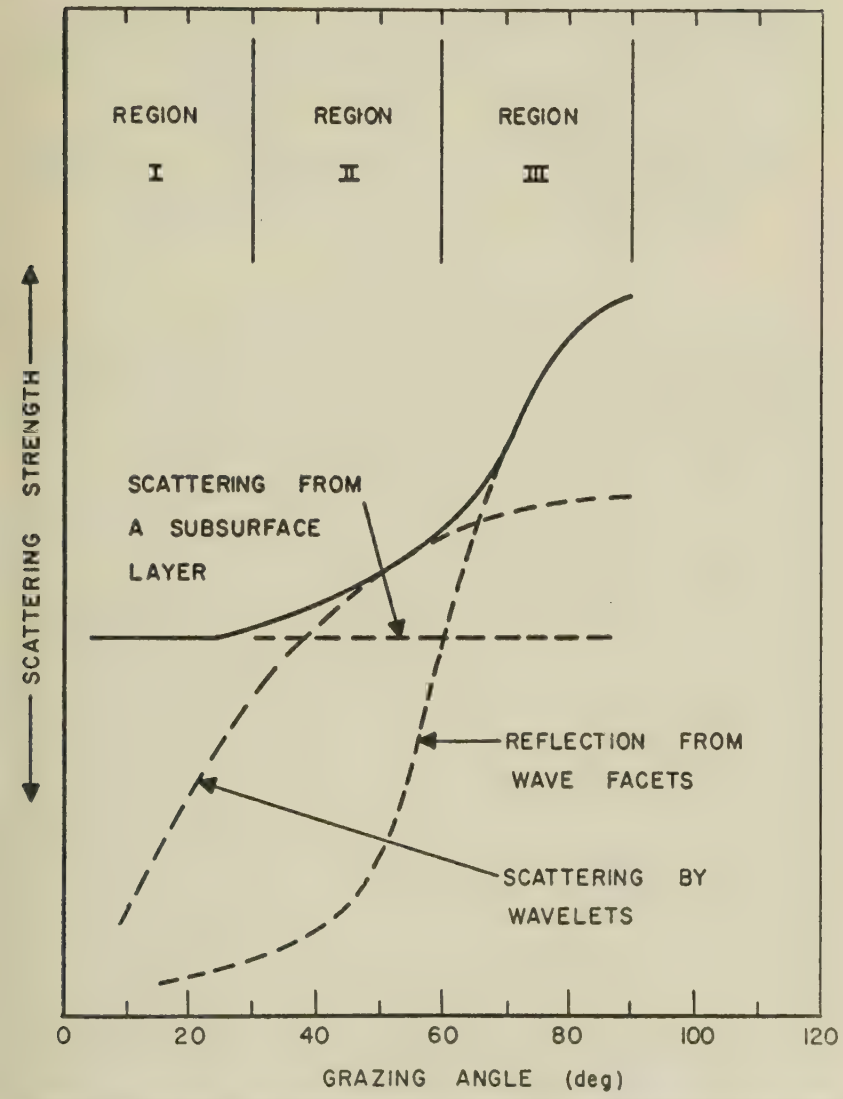

Figure 10. Summary of processes advanced as explanations for observed curves of scattering coefficient as a function of angle.

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QUANTITATIVE EFFECT OF THE SUN'S POSITION ON SUBMARINE LIGHT POLARIZATION[1]

By

TALBOT H. WATERMAN and WILLIAM E. WESTELL

Department of Zoology, Yale University, New Haven, Connecticut
and the Bermuda Biological Station, St. George's West, Bermuda

ABSTRACT

Over 1,000 measurements of the degree and plane of submarine light polarization have been made in littoral waters at depths of 3 to 41m. Using special polarimetric instruments, these parameters were visually measured mainly in horizontal lines of sight at times ranging from sunrise to sunset. Tests showed that observational errors were within $\pm$ 5° for the polarization plane, $\pm$ 5% for per cent polarization.

In every case underwater illumination was linearly polarized (about 5% was threshold for the polarimeter). Determined independently with both *e* and *h* vectors, the plane of polarization changed with solar altitude in a manner that gave a highly significant correlation with the calculated submarine direction of the sun's rays. These effects were greatest at 90° to the solar bearing. With alterations in the latter function, the polarization plane underwent trigonometric variations in orientation with a 360° period. Rates of variation were maximum at 0° and 180° relative to the sun; there the plane of polarization was horizontal. Amplitude of these variations varied inversely with solar altitude, being 0 when this was 90° and greatest when it was 0°. Within the errors of observation, the angle between the polarization plane (*e* vector) and the horizontal was demonstrated to be the same as the sunlight's computed angle of refraction. When the sun was partially or wholly obscured, these relations were modified in ways depending on meteorological optic conditions not yet studied adequately.

Figures for per cent polarization ranged from 5–50% with a variance far greater than the errors in observation. Solar altitude did not affect the degree of polarization in directions 90° to the sun's bearing but it did appear to limit the maximum polarization in the solar bearing itself. This limitation roughly paralleled the prediction based on the angle between the sun's refracted rays and the underwater line of sight. The degree of polarization changed systematically with a period of 180° as the solar bearing altered.

Qualitative data from these and earlier results indicate that turbidity and bottom reflection decreased the degree of polarization. But photometric determination of extinction coefficients and bottom reflection in the present work did not reveal any simple correlation with the polarimetric results. This undoubtedly was due to the great spatial and temporal variations in turbidity which occurred in the littoral areas studied and to the fact that reflected light from the bottom had only 5–15% of the intensity of the penetrating light. Rather extensive measurements in hydro-

[1] Contribution No. 191 from the Bermuda Biological Station.

graphically more uniform water masses will be required to analyze the important factors effectively.

Since several parameters of the underwater polarization pattern show high degrees of correlation with the angle of refraction of sunlight underwater, the sun's position could be determined closely from this pattern. If aquatic animals, like some terrestrial ones, can perceive polarized light, then it has been shown that this ability provides a mechanism for the underwater use of the sun's position in a kind of celestial navigation. Previous data have strongly indicated such a possibility; the present work sustains it and provides the basis for a more quantitative understanding of certain parameters involved.

INTRODUCTION

In lines of sight outside the critical angle with the surface, the polarization patterns of submarine light appear to result largely from the scattering of directional underwater illumination (Waterman, 1954). When the sun is shining on the sea surface, its bearing and altitude will be the main factors which establish the directionality of light penetrating the water. Consequently the sun's position in the sky should quantitatively determine the basic patterns of polarization in submarine light when the firmament is clear.

Previous measurements have shown that this generality seems qualitatively sound, both in shallow and deep water (Waterman, 1955). The present report describes the results of further observations in shallow water where both the amount and the plane of polarization have been quantitatively measured in the field over a wide range of the sun's bearing and altitude. Such information is of interest not merely in relation to the general questions of light penetration and underwater optics but also with respect to the biological possibility that aquatic animals may use a polarized light sun compass (Waterman, 1957).

METHODS

The work reported here was carried out with the aid of aqua-lungs at 20 littoral stations in or near St. Thomas, U. S. Virgin Islands, and at 15 stations in Bermuda. The bulk of the present data comprises those taken in Bermuda, since the greater part of the St. Thomas measurements has been described elsewhere (Waterman, 1957). In the Virgin Island series of stations, data were collected by the senior author. In Bermuda the underwater measurements reported here were carried out by the junior author in collaboration with Mr. Richard Sheffield, to whom our grateful thanks are due. The authors are also much indebted to Mr. Gerald F. Oudens who prepared the illustrations.

Instrumentation. To characterize the pattern of underwater light polarization, use was made of two special polarimetric devices which have been described in detail previously (Waterman, 1955, 1957). The first of these, an interference analyzer devised by the senior author, permitted the following to be determined by inspection: 1) presence or absence of polarized light (with a threshold at about 5% polarization), 2) type of polarization (*i.e.* linear, circular, or elliptical) and 3) orientation of the e and h[2] vectors if linear. For determining orientation, the analyzer was so mounted that a fiducial line could be aligned with either of these vectors and its angle relative to the horizontal read from a calibrated scale.

The second device for measuring the degree of polarization in linearly polarized light was an underwater polarimeter designed and built on the senior author's specifications by Baird Associates of Cambridge, Mass. It consisted of a split field polarizer with the transmitting axes of the halves oriented at 90°. Between this and the observer another polarizer was placed so that it could be rotated. If this was turned until the two halves of the field appeared to be of equal brightness, the degree of polarization, defined as

$$p = \frac{E_{max} - E_{min}}{E_{max} + E_{min}}$$

could be read on a second calibrated scale, provided that one half of the split field polarizer had had its transmitting axis aligned previously with the polarization plane of the light being studied. (In the above expression, E_{max} and E_{min} are the light beam's electrical intensities in the perpendicular planes where this parameter is greatest and least, respectively.)

In practice, then, the interference analyzer provided the data on polarization planes for the submarine illumination and at the same time it automatically oriented the split field correctly for measuring the degree of polarization. An estimate of the accuracy with which this instrument performed in the field may be obtained by comparing independent measurements made in the one case by using for reference the e vector visualized by the analyzer and in the other by using the h vector. Eighty-six pairs of otherwise identical measurements are available in the data for the plane of polarization; these have been plotted in Fig. 1. The correlation coefficient for e and $90°-h$ is 0.9897 and $P \ll 0.01$. More than 95% of the pairs lie well within a band $\pm$ 5° wide.

For the degree of polarization, the 81 available pairs have been

[2] Since the electric field is really concerned here also, this might be more properly called the $e + 90°$ plane.

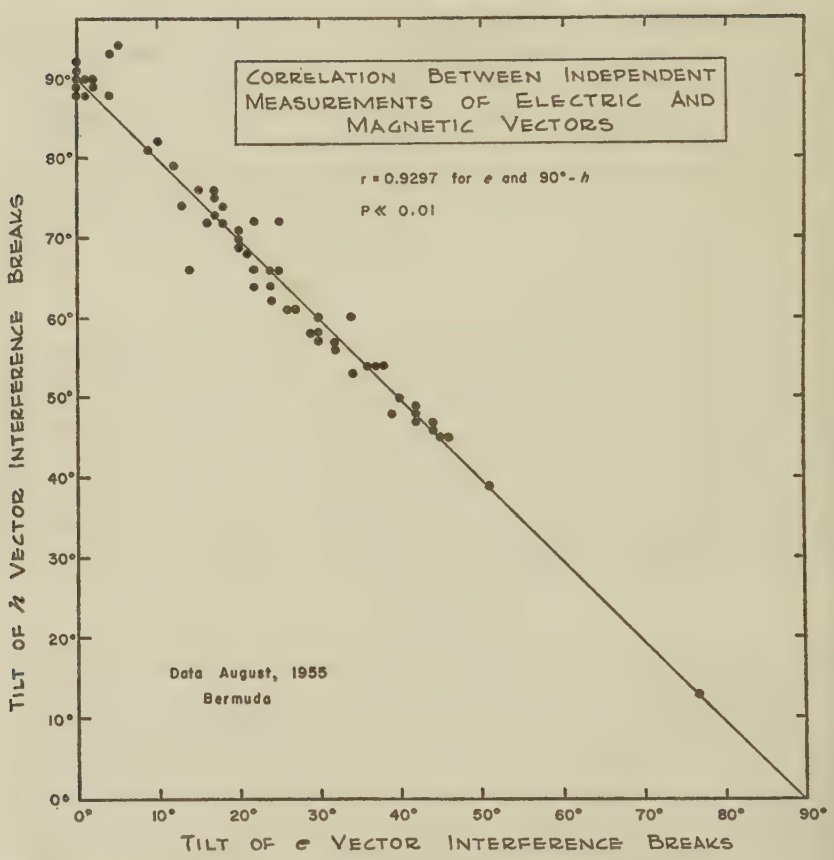

Figure 1. Comparison of polarization planes measured in 86 pairs of observations, one of each being made with reference to the *e* vector, the other to the *h* of the underwater polarized light. Their correlation is strong and highly significant statistically. This treatment of the data indicates the size of the observational errors inherent in the method of measurement as well as the absence of any significant deviation from purely linearly polarized light in submarine illumination in the directions and conditions observed. In this and subsequent figures where individual readings are plotted, all observations are shown except that no attempt has been made to indicate the common occurrence of more than one reading at the same co-ordinate intersect.

plotted in Fig. 2. Their correlation coefficient is 0.9403 and $P \ll 0.01$. Of these paired readings 95% fall within a band 10% wide.

On the basis of this evidence, the polarimetric instruments used in this work provided measurements of the polarization plane with over-all errors generally less than $\pm$ 5° and of the degree of polarization with errors mostly within $\pm$ 5%. The only other apparatus

which has provided underwater polarization data in the field is that which Ivanoff (1956) has described in a short note. This consisted of a Savart plate, an underwater camera and a densitometric calibration to find the degree of polarization; this instrument provides a much less direct method than that used by us. On the basis of the quite limited data so far published for it, this Savart plate-photogrammetric technique does not provide results with less variance than ours.

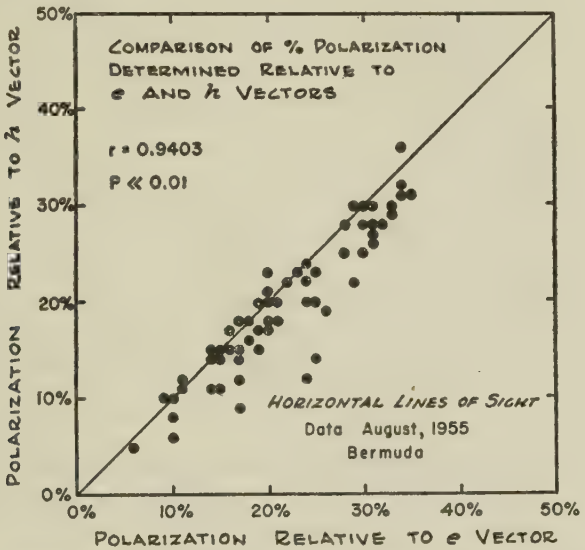

Figure 2. Comparison of degrees of polarization measured in 81 pairs of observations, one each being made with the polarimeter lined up with the *e* vector, the other with the *h* vector. Their correlation is strong and highly significant statistically. This type of analysis indicates the observational errors inherent in the method of measurement with respect to per cent polarization. In this regard it is of interest to compare the variance for this parameter in Fig. 6 where other factors must have been involved in the scatter observed.

Another possible way of determining underwater polarization patterns has been described (LeGrand, 1939), but no published data have resulted from its application.

Procedure. At most stations the procedure in our work was essentially like that described elsewhere for the St. Thomas measurements (Waterman, 1957). The underwater polarimeter was mounted on part of an astro-compass. The latter provided adjustable azimuth and altitude orientation for the optical axis of the system as well as two levelling bubbles for vertical reference. In turn the whole

instrument was placed either on a heavy tripod set on the bottom, or, in a few exploratory measurements, on a vertically floating spar set to support the polarimeter at intermediate depths. Surface distance from the polarimeter was determined with a depth gauge. An underwater compass or a sun sight served for azimuth reference.

In general, measurements of the submarine light polarization were made mainly in horizontal lines of sight referred to the sun's bearing. Most data were taken at 0° or 90° to this reference azimuth, but in a number of cases readings were taken every 45°, sweeping entirely around the horizontal. More usually the *e* vector of the polarized light was used to adjust the polarimeter, but, in a considerable number of cases mentioned above, both *e* and *h* vectors were employed. This procedure permitted an appraisal of the instrumental errors as already cited and it also provided a check as to whether or not under various natural conditions of illumination the interference pattern in the analyzer suffered any distortion from the normal circular shape produced with linearly polarized light.

The sun's altitude and bearing were measured directly with a bubble sextant and compass during the St. Thomas work and in the early part of the Bermuda work. Later, however, the sun's position was plotted from computations made with appropriate navigation tables.

Accessory information collected at each station in Bermuda included: light penetration measurements with a Clarke submarine photometer; bottom reflection data obtained with a Weston photographic light meter in a waterproof case; condition of sky; estimate of underwater visibility; type of bottom; time of observations; and conditions affecting work, such as strong ground swell.

RESULTS

At the 35 stations included in the present report, more than 1,000 measurements of the plane and degree of polarization were made at depths from 3 to 41m at times ranging from sunrise to sunset. In all directions observed and under all conditions recorded, the underwater light was polarized to a degree varying from about 5–50%. Extinction coefficients extended from 0.05 (clear) to 0.185 (turbid) and bottom types from light sand or coral to dark algae and rocks. The resulting information will be presented here mainly in terms of the effect of the sun's position on the underwater polarization patterns. Both the sun's bearing and altitude had important effects not only on the plane of polarization but also on its degree.

Sun's Altitude and Plane of Polarization. When the sun's altitude changed, concomitant modifications in the submarine polarization

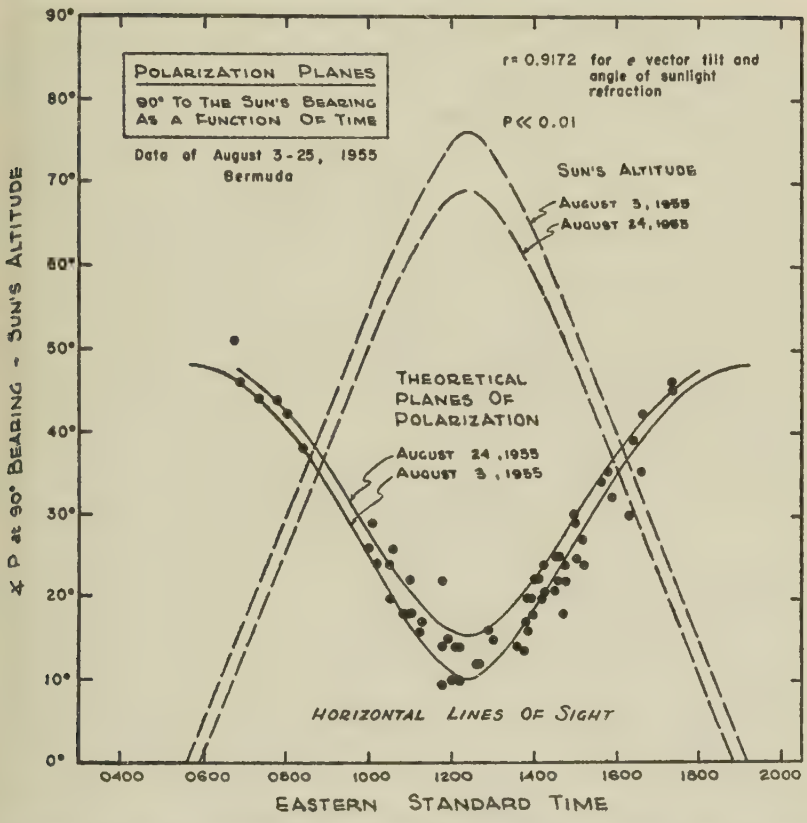

Figure 3. Effect of the sun's altitude on the submarine polarization plane (*e* vector) observed 90° to the solar bearing. This was plotted with time as the abscissa; the 72 individual observations are shown as black circles. For reference the sun's altitude has been indicated by the broken curves for two particular days, one at the beginning and one at the end of the observation period. The calculated angles of sunlight refraction (r) which theoretically would be the same as the *e* vector tilt from horizontal (P; see Fig. 10), have been drawn for the same days (continuous curves). As indicated in the chart, observed planes of polarization and the calculated angles of refraction are strongly correlated in a statistically significant way.

planes took place everywhere except in the bearing of the sun and antisun. Maximum effect of the sun's altitude occurred in azimuths 90° to its bearing. Here the greatest tilt of the *e* vector (defined as the angle between this parameter and the horizontal and measured in 72 cases) occurred at sunrise and sunset while the minimum tilt occurred at local noon sun time (Fig. 3). Conversely, for the *h* vector, which was independently measured in 48 cases in the same

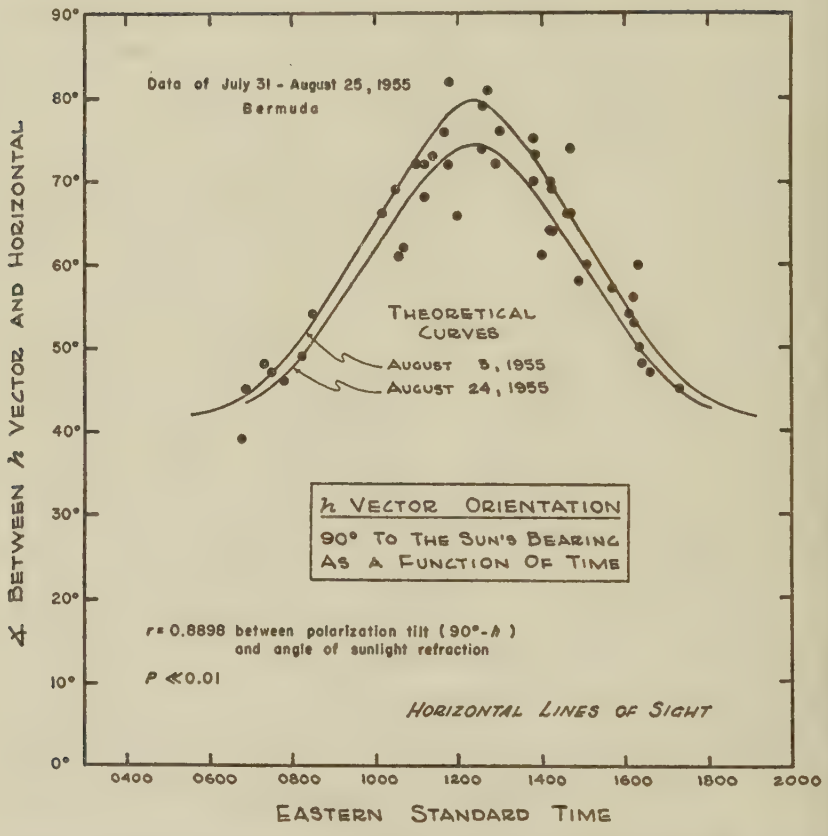

Figure 4. Effect of the sun's altitude on the h vector of the underwater light observed 90° to the solar bearing. The 48 observations and theoretical curves for the h vector orientation based on computed angle of sunlight refraction are plotted as in Fig. 3 except that the h vector has been substituted for the e vector. Again simple theory and observation show a high degree of statistically significant correlation.

direction, minimum tilt, defined in a similar way, occurred early and late in the day with the maximum at noon (Fig. 4).

It can be shown that in both sets of measurements there is a high degree of correlation between the tilt of the polarization plane and the computed angle of refraction of the sun's rays in the water. Theoretical curves to illustrate this fact have been included in both Figs. 3 and 4. These were obtained in the following manner. It is known from Snell's law that the sine of the angle of refraction is numerically equal to $\frac{3}{4} \cos \alpha$, where α is the solar altitude and the refractive index

of the water is taken as 1.33 (see Fig. 10). From this relation one can readily compute the angle of refraction from solar altitudes as a function of time of day. These are also shown in Fig. 3 for two days near the beginning and end of the measurement period; the theoretical curves were derived from these relations. Obviously there is a high degree of similarity between the polarized light planes observed in the field and the calculated refractive angles of underwater sunlight. Correlations were as follows: for the e vector data, $r = 0.9172$, $P \ll 0.01$; for the h vector, $r = 0.8898$, $P \ll 0.01$.

An apparent exception to these general relations was found on one occasion when the sun was 2° above the horizon. The tilt of the e vector at that time was 77°[3], which is far greater than the theoretical maximum angle of refraction. By the time the sun had reached an altitude of 10°, the polarization plane measured 51°, which could have been within a reasonable error from the theoretical curve. Further work will be required to test the reality of this horizon sun condition; if sustained, the causes of such a break from the general picture must be sought.

The foregoing data were obtained with the sun full out. When the sun was completely obscured, marked changes in the planes of polarization occurred so that the underwater pattern came to resemble that which occurred with the sun in the zenith, as previously described (Waterman, 1954). Naturally, such changes were more acute the lower the solar altitude. With haze and with the sun otherwise partially obscured, pattern modifications in the same direction were found regularly, but their degree was markedly dependent on the particular conditions of the moment and was not studied in detail. Much more extensive meteorological optic information would need to be collected and correlated with underwater polarization before more than broad generalizations can be made.

Sun's Bearing and Plane of Polarization. When the sun was at a given altitude, it was found, as before, that the plane of polarization varied systematically with the bearing of the line of sight. Quantitatively this variation in tilt of the e vector was a trigonometrical function, being 0° in the sun's and the antisun's bearings and furthest from horizontal 90° from these bearings. Examples of three stations where the plane was determined every 45° in horizontal lines of sight are shown in Fig. 5; tilt right and tilt left are distinguished on the ordinate. It is clear from this plot that changes in the polarization plane with the bearing are unique at all points around the compass.

[3] This point does not appear in Fig. 3 because it was off scale, but it was included in the analysis which determined the correlation coefficient and its reliability.

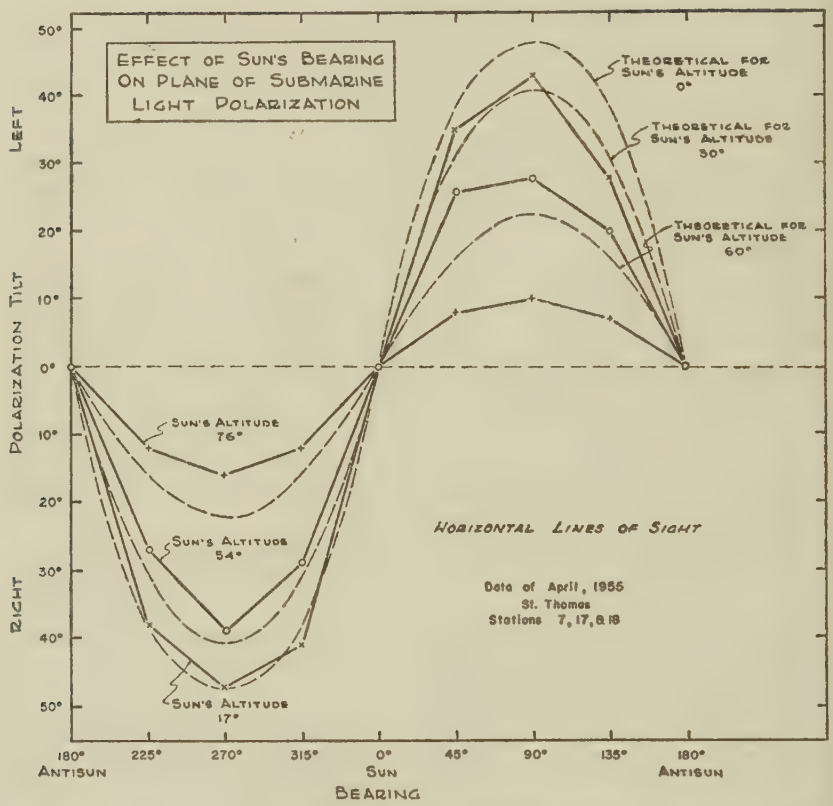

Figure 5. Effect of the sun's bearing on the submarine polarization plane (e vector) observed at three different solar altitudes. Observations are indicated by circles and crosses connected by solid lines. For comparison some theoretical curves (broken lines) computed from the angle of sunlight refraction have been included. The relation used in calculating the curves was $\tan P = \tan r \sin \theta$, where P is the angle between the e vector and the horizontal, r is the angle of sunlight refraction computed from the solar altitude, and θ is the angle between solar bearing and line of sight. Although enough data for statistical treatment are not at hand, agreement between simple theory and observations is good.

Also Fig. 5 illustrates further the effects of the sun's altitude on this phenomenon, since the three stations were made at quite different solar elevation angles, as labelled.

Like the case of the influence of the sun's altitude alone on the polarization plane, the effects of bearing appear to correlate well with the calculated angle of sunlight refraction in the lines of sight concerned. This is demonstrated by the theoretical curves, also drawn in Fig. 5, where the function concerned is described in the

egend. It is quite apparent that there is good basic agreement here lespite the fact that a statistically impressive number of replications ave not been made for a given set of conditions.

As would be expected from the results given above, haze and partial loud cover over the sun altered the pattern of polarization planes versus bearing in the same direction as increased solar altitude. Again however, the specific changes appear to be related to detailed onfigurations and densities of clouds; their analysis must await urther work.

Sun's Altitude and Degree of Polarization. Interestingly enough, anges in the solar altitude had appreciable effects on the degree

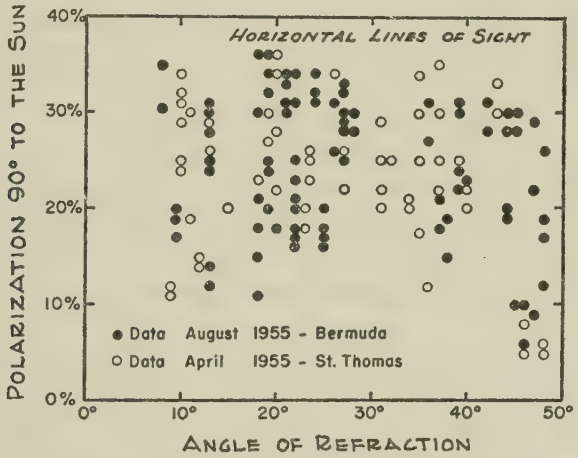

Figure 6. Relation of the sun's altitude to per cent polarization in lines of sight 90° o the solar bearing. Obviously no correlation was present and the scatter of the observed oints was high. This large variance probably arose from the wide fluctuations in turbidity ccurring both spatially and temporally in the littoral waters concerned.

of polarization in azimuths coincident with the sun's bearing but they had little or no detectable influence at 90° bearings. This was the reverse of the effect of solar altitude on the plane of polarization, where the greatest change was at azimuths 90° to the sun's bearing and where no alteration occurred in the sun's or antisun's bearings. At all solar altitudes except those within a few degrees of the horizon, a wide range of degrees of polarization was found in these directions. Measurements were mainly between 15 and 34%, but their distribution showed no obvious correlation with the sun's altitude or with the angle of refraction of its rays in the water (Fig. 6). In other words, the degree of submarine polarization varied widely in the measure-

ments made, but at 90° to the sun's bearing these variations were not the result of changes in the sun's position.

The only exception to this general rule occurred just at sunrise and sunset when several readings of less than 10% polarization were made. This suggests that under some conditions with low sun, its contribution to the over-all penetrating light was reduced and consequently so was the proportion of directional light. Such dependence

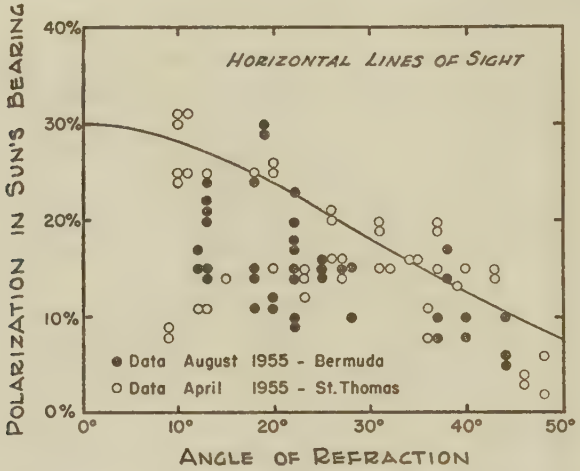

Figure 7. Relation of the sun's altitude to per cent polarization in the solar bearing. As in lines of sight 90° to this (Fig. 6), scatter was large but in this case it seemed subject to an upper limit. The line drawn is a solution for $p = \frac{\sin^2 \theta}{1 + \cos^2 \theta}$, with its maximum point set arbitrarily at 30% to bring the curve within an appropriate range for the data. The rough correlation which is apparent suggests that the computed underwater direction of the sun's rays in relation to the lines of sight was a limiting factor in degree of polarization. No such influence was present where this angle (θ) was constant (Fig. 6).

of the degree of polarization on the directionality of underwater light is sustained by the data in the sun's bearing.

In the solar bearing a quite different set of relations was found. Here the percentage polarization was on the whole less, most of the readings being between 10 and 25%. But in addition, the maximum polarization found was affected by solar altitude and hence by the angle of the sunlight's refraction at the sea surface (Fig. 7). Thus the maximum polarization observed decreased steadily from 30% to 5% or less as the angle of refraction increased from 10°–48°.

Some theoretical correlation for this finding may be found in Rayleigh's well known expression for the degree of polarization due to

light scattering by isotropic particles, small in relation to the wavelength of light:

$$p = \frac{\sin^2 \theta}{1 + \cos^2 \theta}$$

where θ is the angle between the light rays being scattered and the line of sight. If this is solved for the angles of refraction observed in the sun's bearing, the solid curve in Fig. 7 is obtained, provided the maximum p is arbitrarily set at 30% to bring the curve into the general range of the observations.

Admittedly this correlation can be tested only crudely with the present data, yet it is suggestive of a valid limiting function. Note that in the case of azimuths 90° to the sun, θ in the above equation would be invariant with the angle of refraction. Consequently the observed lack of correlation between the sun's altitude and the degree of polarization in that direction (Fig. 6) is consistent with this analysis.

Solar Bearing and Degree of Polarization. With changes in the sun's bearing, the degree of polarization underwent systematic alterations with a 180° period (Fig. 8). Maximum polarization occurred in azimuths 90° to the solar bearing, minimum polarization in direc-

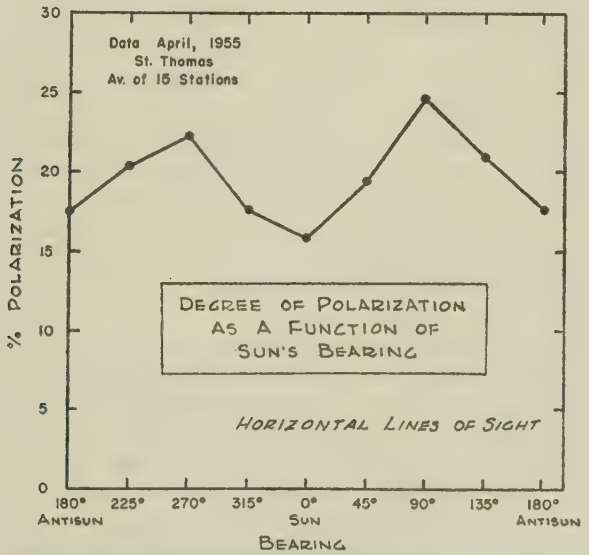

Figure 8. Effect of solar bearing on degree of polarization. The period for this function is 180°, but the large variance in the data (Figs. 6 and 7) probably is responsible for the nonsymmetrical lack of smoothness in the curve.

tions toward or away from the sun, with intermediate p's between these points. In view of the large variance in these data, as demonstrated in Figs. 6 and 7, smooth and significant average curves for this function were not readily forthcoming, although the basic phenomenon was easily observed qualitatively (Waterman, 1954). In the 15 stations averaged for Fig. 8, changes in the sun's bearing effected systematic changes in polarization 5–10% in extent.

On the basis of the analysis used in the preceding section, this fluctuation can be interpreted essentially as due to alterations in θ with changes in the line of sight. At the maximal points the per cent polarization was determined by a number of factors independent of the sun's altitude, whereas at all other azimuths the solar altitude influences the outcome, its effect being greater the lower the sun in the sky.

Other Data Related to Degree of Polarization. Since the recent work on polarization of scattered sunlight in the atmosphere has quantitatively demonstrated the importance of the turbidity of the air and the albedo of the earth (Chandrasekhar and Elbert, 1954; Sekera *et al.*, 1955), the comparable underwater functions are of considerable interest. Decreases in the degree of polarization resulting both from greater bottom reflection and from increased turbidity have already been reported elsewhere for the St. Thomas data (Waterman, 1957).

In the Bermuda measurements some factors widely affecting polarization per cent obviously were at work. Yet it is not possible at this time to account for them quantitatively A long series of light penetration measurements was made along with those on polarization. These have been plotted and extinction coefficients estimated on their basis. The latter show a strong variation ranging from 0.05 to 0.185. Such fluctuations occurred not only within short limits of time at a given station but also at different depths in the water column at the same time. Essentially similar results have been reported for other turbid inshore waters (Burt, 1955b).

Marked local changes in the extinction coefficient due to varying amounts of suspended matter in the water would be expected to have great influence on the degree of secondary and higher order scattering. This in turn would reduce the amount of polarization caused by primary scattering. In addition, the shape, size and other optical properties of the suspended material could change the scattering pattern and hence the polarization in characteristic complex ways (Atkins and Poole, 1952, 1954; Jerlov, 1953; Burt, 1955a; Lenoble, 1956). But the present data do not provide enough information to determine what these were in the present case. Obviously, with

rapid large fluctuations in the extinction coefficient, a large body of data with replicated readings made with the same sun's position and meteorological conditions would be required for effective analysis of its influence on polarization.

The St. Thomas measurements demonstrated a definite effect of turbidity on polarization (Waterman, 1957). However, no significant correlation of this sort can be shown in the quantitative data of the Bermuda results. Curiously enough, the only relationship between per cent, polarization and turbidity in the present data emerges from underwater divers' qualitative observations on submarine visibility conditions. For each station, notes were made on the clarity of the water in terms of the estimated limiting distance at which constant visual definition was possible. These were subjectively classified as: *A*, very clear; *B*, moderate visibility; *C*, poor visibility; and *D*, very turbid. When the resulting judgments were compared with the degree of polarization at 90° to the sun's bearing, the per cent polariza-

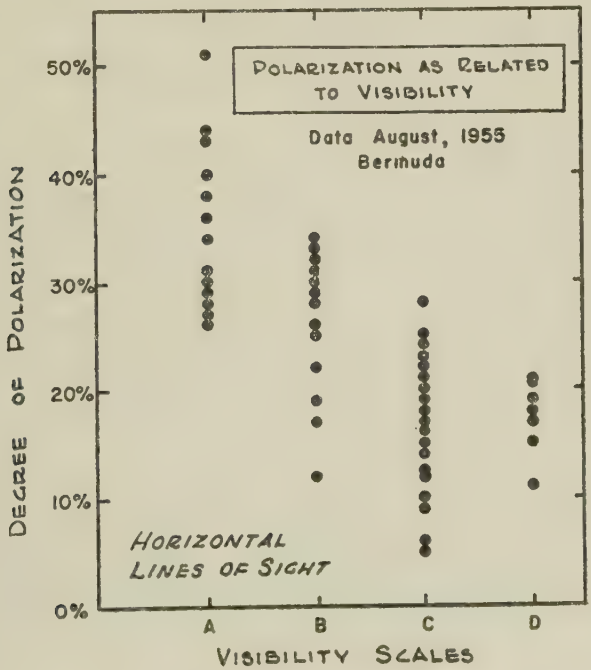

Figure 9. Qualitative evidence for the dependence of per cent polarization 90° to the solar bearing on some transparency factors of the water mass. Data plotted as a function of four arbitrary steps in an underwater visibility scale where *A* indicates *very clear*, *B moderate visibility*, *C poor visibility*, and *D very turbid*.

tion showed a definite correlation with the apparent clarity even though the distribution of points presented considerable overlap (Fig. 9).

It seems likely that further study of this whole problem would be pursued with greater profit where local hydrographic conditions provide water masses which both spatially and temporally are more uniform in their optical properties. In this connection, laboratory study of the influence of various suspended particles, including dense plankton suspension, should be of assistance in analyzing the field problem (e.g. Burt, 1955a). Some exploratory measurements of such phenomena in relation to polarization by algal suspensions have been made by Dr. E. P. Geiduschek of the Yale Chemistry Department and the senior author through use of a light-scattering photometer. As might be predicted, the results were complicated, and further study will be required before an effective analysis can be made.

As in the case of the transparency data, the Bermuda measurements of bottom reflection do not show any obvious correlation with the degree of polarization. Such a correlation has been found in the St. Thomas results (Waterman, 1957); its absence here is undoubtedly due in part to the great variance in the turbidity of the water, which could have had a predominant effect.

The Bermuda measurements with a floating spar as a mount for the polarimeter were planned to reduce or eliminate the influence of bottom reflection by making the observations at intermediate depths away from the bottom. Perhaps the expected advantage of this procedure was demonstrated when it provided the maximum degree of underwater polarization so far measured under any conditions. This was a reading of 51% in Castle Roads with the polarimeter at 8m depth over a dark coral bottom at 14m. In use, however, difficulties with the azimuth reference and with other problems of handling the spar made it impractical to carry out extensive measurements in this way; therefore almost all of the data were obtained with the polarimeter attached to a tripod that was firmly set on the bottom, and thereby more subject to its optical influence. However, examination of light penetration and reflection measurements indicates that only 5–15% of the light was reflected. This finding suggests that, under the conditions encountered in the Bermuda measurements, this factor would have had a relatively minor effect any way.

DISCUSSION

Insofar as theoretical treatment can be applied to the present findings, a number of the major properties of the polarization patterns of submarine light can be accounted for in terms of the calculated directionality of the sun's rays in the water. Both plane and degree of polarization have been found to be quantitatively amenable to

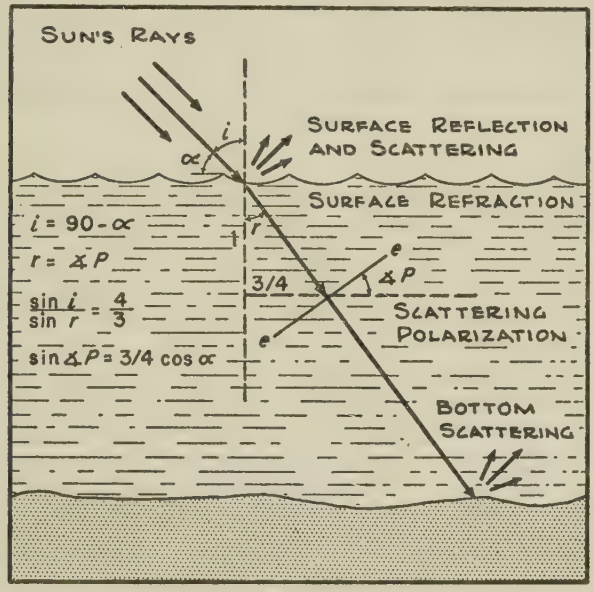

Figure 10. Diagram illustrating the path of sunlight and main factors relating to polarization which influence it in entering and penetrating the sea as seen from a direction 90° to a vertical plane through the sun. The geometrical relation of the polarization plane (*e* vector) to the direction of underwater sunlight, quantitatively supported by the present data, is also indicated. The more general case where the lines of sight are not necessarily perpendicular to the solar bearing nor necessarily horizontal is considered in the legend for Fig. 12.

such analysis, at least to some degree. The basic geometry is diagrammed in Fig. 10.

Conversely, it is clear that the sun's position in the sky can be determined from an examination of the underwater polarization pattern. Unless the sun is too close to the zenith, the solar bearing may be readily located by finding the line of sight with the horizontal polarization plane. The antisolar azimuth can be distinguished from the bearing desired by the directions of tilt at adjacent points (Fig. 5). The decrease in the polarization plane tilt in the sun's bearing is sharp on either side of this point when solar altitudes are

not near 90° (Fig. 11). Such sharp decreases and hence definition of the solar bearing will occur not only in horizontal lines of sight but with elevated or depressed directions of observation, too (Fig. 12).

Similarly the sun's altitude can be measured by estimating the polarization tilt in any directions that are not in the bearing of the sun or antisun. Most accurate inferences would be derived from the polarization pattern at 90° to the solar bearing. It is clear then that basic information is at hand in underwater polarization planes for

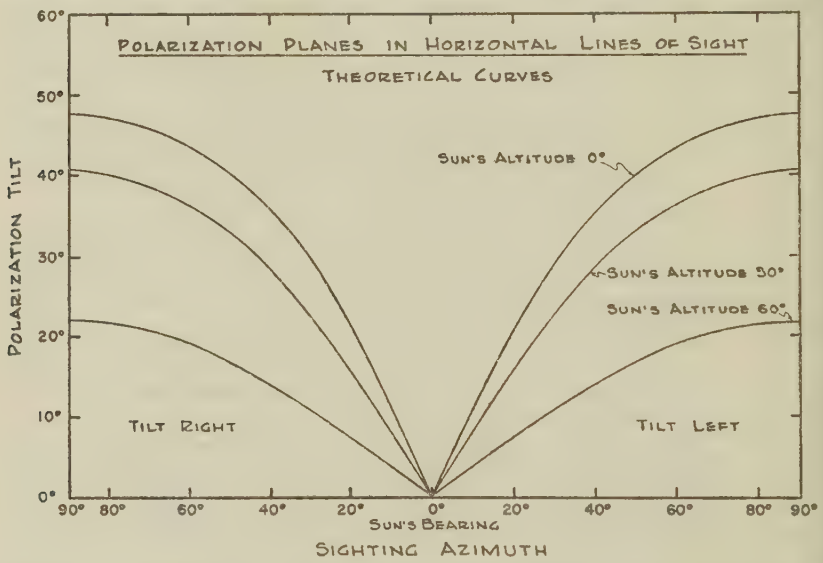

Figure 11. Illustration of the theoretical relations between polarization planes and horizontal sighting azimuth for various solar altitudes. These have been drawn to emphasize the way an aquatic animal which is able to detect and analyze polarized light could use it readily to locate the sun's bearing.

a kind of celestial navigation to be practised by any aquatic animal that can detect and interpret it.

The degree of polarization would offer less reliable information concerning either bearing or altitude of the sun. Over and above the instrumental error (± 5%) in the present determinations, there were the large fluctuations observed in this parameter (Fig. 6) for which no simple correlation was found. The plane of polarization, on the other hand, was definitely related to the sun's position within the range of errors arising from the present instrumentation and observation (5°). At this time it is uncertain how much more closely the angle of refraction, calculated from the sun's altitude and for a

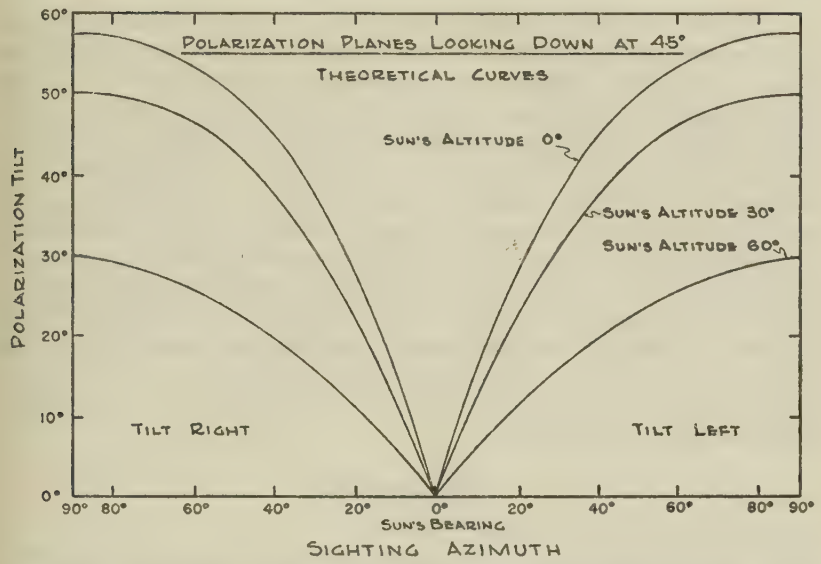

Figure 12. Same relations as in Fig. 11 recalculated for lines of sight depressed 45° from the horizontal to demonstrate that the sun's bearing would be quite obvious not only in horizontal lines of sight but also over a wide range of other directions of view. The curves were drawn on the basis of the general relationship $\tan P = \tan r \frac{\sin \theta}{\cos \gamma}$, where P, r, and θ are defined as in the legend for Fig. 5 and where γ is the elevation or depression of the line of sight from the horizontal. In Figs. 5 and 11 $\cos \gamma$ was 1 since lines of sight there were horizontal.

flat sea surface, and the plane of polarization are in fact correlated. The probable influence of changes in refraction within the water mass, specular reflection from the bottom, interactions of scattering and absorption (Waterman, 1955), and the optical influence of the normally rough surface of the water (Cox and Munk, 1955) are all second order effects which might be found important. Improved instrumentation and more extensive measurements will be required to determine the ultimate limits of the basic correlation demonstrated.

There are abundant facts testifying that sun compasses and the chronometric ability necessary for their operation are widespread in the animal kingdom (Matthews, 1955; Medioni, 1956). It is likewise well known that many terrestrial arthropods can perceive and orient to naturally occurring polarized light, but knowledge concerning behavior of this kind is scanty or lacking for aquatic organisms (Waterman, 1957). Further study in this field of sensory physiology and comparative ethology is acutely needed.

From what we know already, there are numerous questions which must be answered before sound understanding can be developed. In terms of visual function, for example, the mechanism of polarized light detection is paramount. Until it is understood, the means by which orientation to a submarine polarization pattern might take place is obscure. Also the question of whether the lesser degree of polarization in water, compared with the clear atmosphere, is high enough to be of practical use in aquatic vision has not yet been adequately answered. Finally the influence of great depth which reduces the changes in polarization due to the sun's movement (Waterman, 1955) and the transient effects of local meteorological conditions discussed above are most important matters on which knowledge needs to be extended. If polarized light navigation can be demonstrated in the field for aquatic animals, all these basic problems must be effectively solved.

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THE POTASSIUM-CHLORINITY RATIO OF OCEAN WATER

By

RALPH E. JENTOFT[1] AND REX J. ROBINSON

Oceanographic and Chemical Laboratories
University of Washington
Seattle, Washington

ABSTRACT

A method for determining the amount of potassium in ocean water has been described. With this procedure, a number of ocean water samples have been analyzed for potassium, and the potassium-chlorinity ratios have been calculated. The ratio has been found to have a constant value of 0.02023 with a standard deviation of 0.000,032 or 1.6 parts per 1,000.

INTRODUCTION

Ocean water is a complex solution of many ions, among which the chloride ion is predominant. It has been shown that the relative concentrations of the major ions bear a surprisingly constant ratio to one another even though the total concentrations of ions vary from place to place in the oceans. In Table I the ion-chlorinity ratios of some of the major ions in sea water are tabulated for comparative purposes. The potassium-chlorinity ratio is not listed because of the variability of previous results which probably resulted from difficulties of analysis for potassium.

In Table II are summarized the estimates of the potassium-chlorinity ratio based upon the analyses of various investigators since 1880. These results are subject to criticism because of uncertainties in the methods of analysis, use of erroneous atomic weights, lack of correction for air buoyancy in weighing and use of an improper reference standard for chlorinity. It appears that Dittmar's ratio for potassium carries the most weight among these values because his early work on the composition of sea water in general has proven to be quite reliable and is an accepted reference where more recent work is in doubt. Lyman and Fleming (4) also arrived at a value of 0.02029 for Dittmar's ratio after correcting for air buoyancy in weighing, for the reference standard used for chlorinity and for changes in atomic weights.

[1] Present address, California Research Corporation, Richmond, California.

TABLE I. The Ion-Chlorinity Ratios of Some of the Major Ions in Ocean Water

Ion	*Chlorinity Ratio*	*Precision*[a] (‰)	*Authority*
Sodium	0.5556	2	Robinson and Knapman (7)
Sulfate	0.1394[b]	2.4	Thompson *et al.* (10)
Magnesium	0.06695[b]	1.6	Thompson and Wright (11)
Calcium	0.02150	2.9	Thompson and Wright (11)

[a] These values are the standard deviations of the results published in the literature.

[b] These values have been corrected for air buoyancy in weighing, for the reference standard used for chlorinity, and for changes in atomic weights as specified by Wichers (14).

TABLE II. Previous Values for the Potassium-Chlorinity Ratio of Ocean Water*

Author	*No. of Samples*	*Location*	K/Cl†
Schmelck (1882)	6	N. Atlantic	0.02026‡
Forsberg (1883)	4	Siberian	.0211‡
Dittmar (1884)	77	All oceans, except Polar	.02029‡
Natterer (1892–4)	57	Mediterranean	.02008‡
Kolotoff (1893)	1	Black Sea	.0210‡
Makin (1898)	22[a]	Atlantic	.02036‡
Macallum (1903)	3	Atlantic	.02025‡
Schloesing (1906)	3	Atlantic, Mediterranean	.01953‡
Wheeler (1910)	5	Atlantic	.0263‡
Steiger (1910)	1	Atlantic	.01988‡
Anderson and Thompson (1929)	12	Puget Sound	.0191‡
Webb (1939)	1	Atlantic	.02009
Miyake (1939)	1[a]	Pacific	.0191

* Compiled chiefly by Webb (13).

† In most cases in which the method is described, the potassium was precipitated as chloroplatinate and was weighed either as such or more usually converted to platinum. Exceptions are the method of Webb, in which potassium silver cobaltinitrite was precipitated and titrated, and the method of Anderson and Thompson, in which potassium perchlorate was precipitated and weighed.

‡ Calculated by Webb (13) from the published analyses. The results of Dittmar and of Makin were corrected for changes in atomic weights. Natterer's ratios were corrected by reckoning bromide as chloride as in all other analyses.

[a] All the samples were pooled together to make one composite sample.

The present study arose from a desire to establish the potassium-chlorinity ratio with certainty. The analyses for potassium were performed by the method of Jentoft and Robinson (2), in which the potassium is precipitated as the metaperiodate and then estimated iodimetrically. This method is a modification of that originally reported by Willard and Boyle (15).

PROCEDURES

The chlorinities of the various ocean water samples were determined by the well known Mohr procedure as adapted to oceanographic analyses.

The theoretical considerations involved in the iodimetric determination of potassium as the metaperiodate have been discussed elsewhere by Jentoft and Robinson (2). The procedure for the analysis of potassium used in the present investigation is as follows:

Measure 25 ml sea water sample into a 100 ml beaker. Then add 0.2 ml of a 0.1% gelatin solution and 1.0 g of solid sodium cobaltinitrite and stir the solution until the sodium cobaltinitrite has dissolved. Cool the solution to about 0° C in an ice-bath, add 25 ml of 95% ethyl alcohol and refrigerate the solution at 0° C for eight hours. Filter the solution through a Gooch crucible and wash the precipitate and beaker once with 95% ethyl alcohol cooled to 0° C. Evaporate the alcohol completely on the steam bath and then dissolve the precipitate in 10 ml of hot 5 N nitric acid. (*Failure to evaporate the alcohol completely may result in an explosion when the nitric acid is added and heated.*) Next render the cobaltous ion inactive by precipitating with 10 ml of oxalic acid reagent. Then evaporate the solution to dryness on the steam bath.

Add exactly 2 ml of water to the dry sample to dissolve the potassium and then precipitate slowly with two 0.5 ml portions of periodic acid, spaced 10 minutes apart. Stir the solution occasionally after adding the reagent. Ten minutes later add 0.4 ml of lithium acetate solution, with rapid stirring, at the rate of about one drop (0.02 ml) per second. After 10 minutes add the lithium acetate reagent as before until the added 2, 6-dinitrophenol indicator turns dark yellow in color, indicating a pH of 3.0 to 3.5. Usually about 0.6 ml of lithium acetate is required in the second addition. Add two ml of 95% ethyl alcohol to the solution and cool the precipitate and solution with frequent agitation for 30 to 45 minutes in an ice-bath. Then decant the solution through a previously cooled 10 ml Gooch crucible prepared with a single-layer asbestos mat. Wash the precipitate with a 2–1 ethyl alcohol-isopropyl alcohol wash liquor also cooled to 0° C; the beaker

should be washed 4 to 5 times and the crucible 5 to 7 times, depending upon the amount of solids present.

Dissolve the potassium metaperiodate in 10 ml of 4 *N* sulfuric acid diluted with 25 ml of water. Add solution containing 1 g of potassium iodide and titrate the liberated iodine with standard sodium thiosulfate solution, using starch as the indicator. The equivalents of potassium are equal to one-eighth the equivalents of sodium thiosulfates used. The reactions involved are

$$H_5IO_6 \leftrightarrows H_4IO_6^- + H^+ \leftrightarrows IO_4^- + 2\,H_2O \quad (1)$$

$$K^+ + IO_4^- \rightarrow KIO_4 \quad (2)$$

$$KIO_4 + 7\,I^- + 8\,H^+ \rightarrow K^+ + 4\,I_2 + 4\,H_2O \quad (3)$$

$$I_2 + 2\,S_2O_3^{-2} \rightarrow S_4O_6^{-2} + 2\,I^- \quad (4)$$

REAGENTS AND SOLUTIONS

Reagent grade chemicals were used throughout this investigation unless otherwise stated.

Ammonium Molybdate. Prepare 3% ammonium molybdate solution to catalyze the reaction between bromate and iodide in acid solution according to the recommendation of Kolthoff and Sandell (3 p. 594).

Asbestos. Digest a good grade of asbestos with concentrated nitric acid for four hours, filter and wash with distilled water. This treatment is necessary to prevent retention of periodic acid which could not otherwise be washed free of the asbestos, causing high results.

2,6-Dinitrophenol. Prepare a 0.1% solution of 2,6-dinitrophenol by dissolving in water with the aid of an equivalent amount of lithium carbonate.

Gelatin. Prepare a 0.1% gelatin solution by dissolving granular gelatin in water saturated with mercuric iodide which will serve as a preservative.

Lithium Acetate. Prepare a 2.5 N lithium acetate solution by dissolving 18.5 g of purified lithium carbonate in 30 ml of glacial acetic acid and diluting to 200 ml.

The lithium carbonate was purified by double crystallization. Lithium carbonate was suspended in water and dissolved in a stream of carbon dioxide. The solution was filtered and the lithium carbonate was reprecipitated by heating the solution to the boiling point until evolution of the carbon dioxide was complete. After the second crystallization the lithium carbonate was dried at 120° C for 24 hours.

Organic Solvents. Redistill the ethyl and isopropyl alcohols before using, retaining those fractions which distill within a range of 1 to 3° C. Prepare a 2–1 ethyl alcohol-isopropyl alcohol wash liquor from these.

Oxalic Acid. Prepare a solution to contain 10 g of oxalic acid dihydrate per liter.

Periodic Acid. The periodic acid, obtained from the G. F. Smith Chemical Company, was found to be free of iodic acid by the test described by Willard and Boyle (15). Prepare the periodic acid reagent so that it contains 0.5 g of H_5IO_6 per ml. Since this solution deteriorates on standing, it was prepared fresh as needed.

Potassium Iodide. Make up a solution containing 1 g of potassium iodide per 10 ml of water as needed.

Potassium Iodate. Purify the potassium iodate by recrystallization and dry at 180° C to constant weight according to Scott (8, p. 1209). Prepare a 0.075 N solution on which to standardize the sodium thiosulfate solution.

A similar standard solution of potassium bromate was prepared according to Kolthoff and Sandell (3, p. 594).

Sodium Chloride. Recrystallize the sodium chloride from a saturated solution by precipitating with hydrogen chloride gas. After filtration and washing with distilled water, dry at 390° C for 12 hours.

Sodium Thiosulfate. Prepare an approximately 0.042 N sodium thiosulfate solution and stabilize with sodium furoate according to Platow (6). Add to each liter of solution a filtered solution of 1.0 g of furoic acid and 0.6 g of sodium carbonate.

Standardize the sodium thiosulfate solution against either potassium iodate or potassium bromate each time before using. To a 25 ml portion of standard iodate or bromate solution add 10 ml of 4 N sulfuric acid and sufficient potassium iodide for complete reduction of the oxidizing agent and for solution of the liberated iodine. When using the bromate standard, add 4 or 5 drops of the ammonium molybdate solution to catalyze the oxidation of iodide. Use starch as the indicator when titrating the liberated iodine with the sodium thiosulfate solution.

Sodium Cobaltinitrite. Use solid sodium cobaltinitrite, free of potassium.

Starch. Prepare a starch indicator solution according to Kolthoff and Sandell (3). To a liter of boiling water add a water suspension of 2 g of soluble starch plus 10 mg of mercuric iodide to serve as a preservative. Heat the solution until clear and then filter.

EXPERIMENTAL

The analytical weights were calibrated against Class M weights previously calibrated by the National Bureau of Standards. All weighings involved in the various standardizations were corrected for air buoyancy.

Calibrated Normax volumetric equipment was used in all cases. Standard solutions were calculated to 20° C; when these solutions were used at other temperatures, corrections were made for the changes in the volumes of these solutions.[2] Likewise the temperatures of the ocean water samples at the time of analysis were recorded so that the amount of potassium per kilogram of the sea water could be calculated.

To avoid introduction of errors in the calculated results due to lack of significant figures in the volumes of the sodium thiosulfate solution used, the normality of the titrant was adjusted so that the titration volumes usually fell between 40 and 50 ml. The titrant was always standardized against two independent standard solutions and check values differing by no more than 0.1% were demanded.

The silver nitrate solution, prepared to be about 0.28 N, was standardized against two reference standards. In one case, weighed amounts of recrystallized sodium chloride, dried at 390° C for 12 hours, were used as the standard. A correction factor of 1.00045, as pointed out by Sverdrup *et al.* (9, p. 52) was used for converting the chlorine equivalent to the chlorinity. The other standard was the Normal Sea Water prepared by the Hydrographical Laboratories in Denmark. Results by these two standardizations agreed to within less than 0.005 chlorinity unit. Checks to within less than 0.010 chlorinity unit were demanded in the chlorinity determinations on the sea water samples.

It was found that much of the calcium in the ocean water samples taken for analysis was precipitated as calcium sulfate in the 50% alcohol solution during the precipitation of the potassium-sodium cobaltinitrite. This had no undesirable effect on the subsequent iodimetric estimation of potassium.

The 1952 International Atomic Weights were used in all calculations (14).

DISCUSSION OF RESULTS

The results of the various analyses of sea water samples are presented in Table III. These samples had been obtained from a number

[2] The correction factor was d_t/d_{20}, where d_{20} is the density of water at 20° C and d_t the density of water at the other temperature.

TABLE III. The Potassium-Chlorinity Ratio of Ocean Water

Depth Meters	K ‰	Cl ‰	K/Cl
Labrador Sea, Atlantic Ocean; Lat. 60° 17′ N, Long. 59° 41′ W; April 28, 1950			
1	0.3800	18.878	0.02013
197	0.3894	19.262	0.02022
	0.3889		0.02019
984	0.3897	19.311	0.02018
Gulf Stream, Atlantic Ocean; Lat. 32° 30′ N, Long. 77° 14.5′ W; February 26, 195			
0	0.4039	20.034	0.02016
37	0.4039	20.018	0.02018
	0.4046		0.02021
	0.4036		0.02016
419	0.4036	19.974	0.02021
Sargasso Sea, Atlantic Ocean; Lat. 32° 18′ N, Long. 64° 31′ W; January 13, 195			
471	0.4050	20.082	0.02017
Off Lower California, Pacific Ocean; Lat. 24° 48.5′ N, Long. 116° 40′ W; February 3, 1950			
0	0.3780	18.730	0.02018
200	0.3858	19.106	0.02019
1000	0.3857	19.113	0.02018
Lat. 28° 40.5′ N, Long. 122° 46′ W.			
0	0.3779	18.711	0.02020
200	0.3759	18.639	0.02017
2000	0.3871	19.159	0.02020
Lat. 29° 36.5′ N, Long. 116° 19.5′ W.			
0	0.3758	18.570	0.02024
200	0.3810	18.827	0.02024
	0.3791		0.02014
1200	0.3858	19.116	0.02018
Off Washington Coast, Pacific Ocean; Lat. 47° 25′ N, Long. 126° 17′ W; March 14, 1952			
100	0.3731	18.521	0.02014
1000	0.3844	19.092	0.02013
	0.3851		0.02017
1800	0.3871	19.212	0.02015
Lat. 47° 50′ N, Long. 127° 29′ W; May 2, 1952			
0	0.3659	18.103	0.02021
100	0.3711	18.412	0.02016
1000	0.3847	19.063	0.02018
2000	0.3869	19.143	0.02021

TABLE III (continued)

Depth Meters	K‰	Cl‰	K/Cl
Off Vancouver Island, Pacific Ocean; Lat. 49° 10′ N, Long. 128° 48′ W; May 5, 1952			
1000	0.3802	18.854	0.02017
2000	0.3869	19.130	0.02022
Hein Bank, Strait of Juan de Fuca; Lat. 48° 21.2′ N, Long. 123° 05.7′ W; March 12, 1952			
0	0.3437	17.036	0.02017
10	0.3459	17.145	0.02018
50	0.3478	17.212	0.02021
	0.3468		0.02015
135	0.3563	17.666	0.02017
East Sound, Orcas Island, Washington; Lat. 48° 41′ N, Long. 122° 54′ W; July 10, 1951			
0	0.3278	16.220	0.02021
23	0.3429	16.974	0.02020
Lat. 48° 37′ N, Long. 122° 51′ W; July 10, 1951			
27	0.3458	17.085	0.02024
Off Point Jefferson, Puget Sound; Lat. 47° 45.5′ N, Long. 122° 24.8′ W; March 11, 1952			
0	0.3279	16.248	0.02018
20	0.3312	16.419	0.02017
50	0.3326	16.453	0.02022
100	0.3337	16.537	0.02018
200	0.3342	16.576	0.02016

Mean of all samples	0.02018, S_1[a]	= 0.000,028
Correction	+0.00005, S_1	= 0.000,015
Corrected Ratio	0.02023, S_3	= 0.000,032[b]

[a] S = Standard deviation.

[b] See equation (1).

of widely separated stations in the Atlantic and Pacific Oceans as well as from the inland waters of the Puget Sound Region.

The precision and accuracy of the potassium determination have been evaluated elsewhere by the authors (2). For the amount of potassium (8–10 mg) taken for analysis in a 25 ml sample of sea water, the precision is approximately $\pm$ 0.1% and the accuracy is approximately $-0.25 \pm 0.075\%$. The negative value for the accuracy is significant. It denotes a small systematic solubility error for

which a correction may be applied to experimental results. The value ± 0.075 is the mean deviation of this error.

It has been shown by Jacobsen and Knudsen (1) that a precision and accuracy of about ± 0.05% may be attained with very careful work for the chlorinity determination. The data of the present study support this value; however, to be conservative, we have considered that the chlorinity data of the present work have a precision and accuracy of about ± 0.067%.

In Table III the potassium-chlorinity ratio has been calculated for each sample of sea water. The mean of all ratios and the standard deviation have been calculated to be 0.02018 ± 0.000,028, respectively, with no significant regional differences being evident. This mean ratio has been corrected for the solubility error mentioned above. The corrected potassium-chlorinity ratio of sea water then becomes 0.02023 ± 0.000,032. The new value of the standard deviation, s_x, was calculated from the expression

$$s_x = \sqrt{s_a^2 + s_b^2} \tag{1}$$

where s_x = standard deviation of the sum x; s_a = standard deviation of a; s_b = standard deviation of b, as given by Vignau (12) for the standard deviation of the sum $x = a + b$. The precision (standard deviation) of the corrected ratio, 0.000,032 or 1.6 parts per 1,000, compares favorably with the precisions for the ratios given in Table I; only the ratio of magnesium/chlorinity has as favorable a precision.

It is possible to calculate what the standard deviation of the potassium-chlorinity ratios should be from the established standard deviations for the determinations of potassium and chlorinity. Using the values given previously, the expected standard deviation has been calculated to be 0.000,024 from the expression given by Vignau (12) for the standard deviation of the quotient $x = a/b$:

$$s_x = \frac{\sqrt{(b \times s_a)^2 + (a \times s_b)^2}}{b^2} .$$

This calculated value compares well with the experimental value of the standard deviation, 0.000,028, and indicates that the application of this method to sea water is valid. The precision of these results is as good as or better than that for the ion-chlorinity ratios determined for the other major ions in sea water.

The corrected value of 0.02023 for the potassium-chlorinity determination established in the present investigation agrees closely with the value 0.02029 based on Dittmar's work and corrected by Lyman

and Fleming (4) and Webb (13), but it differs considerably from the values obtained by other investigators listed in Table II.

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